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Development of Silicone Rubbers for Use at Temperatures Down to 100°F 86 846
5 Dec. 1949 to 4 March 1950 (Progress Report) (None)

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(Same)

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A first progress report is presented on a program concerned with the development of silicone rubbers for use at temperatures down to -100°F. At present, work is concentrated primarily on two factors. The first of these is concerned with the nature of the pigment-rubber interface in an attempt to improve the strength of the bond between pigment and rubber. The second is concerned with the nature of the curing reaction and with the investigation of methods of improving this step. The remaining method of attack that might be followed involved the preparation of the gun, which, however, is not yet included in the present program. In the pigment study, some 50 materials were tried as pigments. Wetting agents for the pigment rubber interface were also investigated. The method of curing or cross-linking silicone rubber is under study, one of the most interesting possibilities being the use of selenium dioxide.

*Others Copies obtainable from CADO.

Materials (8) Rubber, Synthetic
Rubber, Natural and Synthetic (3)

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DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F.

U. S. GOVERNMENT CONTRACT DA-44-109-QM-64

FIRST PROGRESS REPORT

FOR THE PERIOD

DECEMBER 5, 1949 to MARCH 4, 1950

MAY 1, 1950

CONNECTICUT HARD RUBBER COMPANY
407 EAST ST.
NEW HAVEN, CONNECTICUT

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CONNECTICUT HARD RUBBER COMPANY NEW HAVEN, CONNECTICUT

DEVELOPMENT OF SILICONE RUBBERS FOR USE AT TEMPERATURES DOWN TO -100°F.

U.S. GOVERNMENT CONTRACT DA-44-109-QM-64

PROGRESS REPORT I

(Covering Experimental Work Performed
During the Period Dec. 5, 1949 to Mar. 4, 1950)

May 1, 1950

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*No experimental work on these factors was included in the period covered by this report.

SUMMARY

The investigation of silicone rubber which is in progress at the laboratory of the Connecticut Hard Rubber Company is at present concentrated primarily on two factors. The first of these is concerned with the nature of the pigment-rubber interface in an attempt to improve the strength of the bond between pigment and rubber. The second is concerned with the nature of the curing reaction and with the investigation of methods of improving this step. The remaining method of attack which might be followed involves the preparation of the gum; this is not included in the present program, although it might be included later.

In the pigment study, some 50 materials of widely varying chemical composition, particle size, particle shape and surface area have been tried as pigments. The properties of the cured stocks vary greatly, the tensile strength range being about ten-fold. The effectiveness of the pigments does not appear to correlate with any of the factors listed above. The marked specificity of the pigment, together with the fact that various pretreatments of the pigments (such as degassing at 1000°C. and 0.0001 mm. Hg, coating with a silicone film, etc.) has little effect on the results, leads to a some confusion regarding the nature of the pigment - rubber bond since such behavior would not be expected of either purely physical or purely chemical bonding. An attempt to determine the factor responsible for the results is being made. A specific attack involves a study of electrostatic charges on the pigments and on the gum.

The effect of variable volume loading has been determined for some of the most promising materials. Stocks containing mixtures of pigments have been compounded and the suggestion is made that the use of pigment mixtures adds a degree of freedom in compounding which might

be useful in later work. A statistical analysis of results on a control stock is reported. The degree of reproducibility is low. The factors which might be responsible for this are noted and some suggestions for improving the reproducibility are made.

Wetting agents for the pigment-rubber interface are being investigated with particular attention centered on silicone analogs of the higher fatty acids, the wetting agents of hydrocarbon rubber practice. One silicone carboxylic acid has been synthesized and tested as a wetting agent. This simple acid, p-trimethylsilyl benzoic acid, appears to provide some improvement in milling time. Other acids are being synthesized.

The electron microscope is being used to obtain information on the pigments and on the pigment distribution in gum. A number of electron micrographs are reproduced in this report to illustrate the results being obtained. Correlation of these results with other results of the program has not yet been attempted but such correlation will be attempted soon.

Attempts have been made to improve the distribution of pigments in the gum by preparation of suspensions containing both the gum and the pigment followed by simultaneous breaking of the suspensions. Wetting agents for such emulsions in water are being sought in the metal salts of silicone carboxylic acids being synthesized for another portion of this program. Another suggestion under investigation involves solution of the gum in titanium tetrachloride followed by hydrolysis of the latter to form titanium dioxide as a pigment.

It has been suggested that the properties of silicone stocks might be improved by removing the lower molecular weight materials from the gum by such processes as solvent extraction. No progress on this investigation has been made during the period covered by this report.

The method of curing or cross-linking silicone rubber is under investigation. One of the most interesting possiblities for creating this cross-link is by the use of selenium dioxide, which has been tried in some preliminary experiments. Another possibility lies in the fact that p-trimethylsilylbenzoic acid, synthesized for another portion of this program, appears to have a curing effect for reasons as yet unknown. The possible use of silicon-containing compounds for curing has the advantage of introducing less heat-sensitive materials in the stocks.

INTRODUCTION

Numerous methods of attack are available in attempting to develop from currently available silicone gums, a rubber product with service characteristics (measured by tensile strength, elongation, abrasion resistance, compression set, etc.) approaching more closely those of hydrocarbon rubbers. To indicate the reasons for the particular methods of attack chosen to be followed in this investigation, there are reviewed below:

1- a general description of the chemistry and techniques involved in current practice in silicone gum manufacture and compounding.

2- a general statement of the basic methods of attack on the problems of improving the properties of silicone rubber stocks, and

3- an outline of the research program in progress at the laboratory of the Connecticut Hard Rubber Company.

Current Practice in Silicone Gum Manufacture and Compounding

Silicone gum is manufactured by the hydrolysis of dimethyldichlorosilane. A study of the available literature indicates that this hydrolysis is probably carried out in two steps. In the first step, dimethyldichlorosilane is carefully poured onto the surface of a propeller-agitated solution of an electrolyte, numerous electrolytes being suitable for this step. The product is a polymeric dimethyl silicone, either cyclic or straight-chain, and is removed from the kettle as an oily liquid. Subsequent treatment of this liquid with a catalyst (iron chloride, for example) results in the formation of the gum. Available information indicates that this gum consists primarily of a linear polymer of the type:

$$
\begin{array}{ccccccc}
 & CH_3 & & CH_3 & & CH_3 & \\
 & | & & | & & | & \\
- & Si & -O- & Si & -O- & Si & -O- \\
 & | & & | & & | & \\
 & CH_3 & & CH_3 & & CH_3 &
\end{array}
$$

It is entirely possible that some cross-linking also occurs in the second stage of the hydrolysis.

To convert the gum to a useful rubber, it is first broken down on a rubber mill. A pigment (such as titanium dioxide, silica or diatomaccous earth) and a curing agent (usually benzoyl peroxide) are incorporated in the gum while it is on the mill. Subsequent curing of molded specimens is believed to involve cross-linking brought about by the benzoyl peroxide. The current theory is apparently derived from an analogy to the behavior of benzoyl peroxide as an agent in the polymerization of diolefins, where it is fairly well established that the polymerization rate is increased because the benzoyl peroxide activates the methylene hydrogen atoms. On this basis, the cross-linking is believed to involve splitting out of two atoms of hydrogen between methyl groups on adjacent silicone chains. The result is an ethylene bridge between the chains.

It may be noted that mechanical mixing of the gum and pigment might be avoided by adding the pigment to the material in the second stage of the hydrolysis. Such a technique would result in more intimate dispersion than could be obtained on a mill.

Basic Methods of Attack in Improving Silicone Rubber

Consideration of the procedures outlined above would indicate that three basic attacks might be used in attempting to improve the properties of silicone rubber stocks. These are:

1- Hydrolysis of $R_2 SiCl_2$

  a. Using alkyl groups other than methyl.

  b. Varying the conditions of hydrolysis.

2- Pigment Studies

  a. Selection of proper pigment

  b. Altering the nature of the pigment-rubber interface

  c. Methods of dispersing the pigment

3- Studies of the curing reaction

a. Use of agents other than benzoyl peroxide

b. Use of activators for benzoyl peroxide

c. Substitution of hydrogen atoms or methyl groups in gum by groups more reactive in cross-linking. This would be accomplished either in the hydrolysis step by using, for example, monomethyldichlorosilane, or by chemical treatment of the gum.

Actually, improvement of the physical properties of silicone stocks is probably going to involve eventually all of the three basic attacks.

It has been decided that for the present the research program in this laboratory will be based primarily on methods (2) and (3) of the above outline. Essentially, this consists in accepting as the immediate task of this laboratory determination of the optimum conditions for using currently-available silicone gums. Though such a procedure might not result in improvement over present techniques, it is essential that such studies be carried out. Developing the present gum to its optimum physical properties is a necessary step in the whole silicone program.

The experimental program now under way is outlined briefly below. Those sections which have received attention in this period are discussed in more detail in the next sections.

Outline of Experimental Program

I. Studies of Pigments

   A. Pigments as-received, 25-volume loading

   B. Pigments after pretreatment, 25-volume loading

   C. Pigments as-received or pretreated, variable volume loadings.

   D. Mixtures of pigments, as-received or pretreated.

   E. Milling techniques.

II. Wetting Agents for Pigment-Rubber Systems

   A. General survey of materials available commercially

   B. Synthesis of silicone carboxylic acids or silicone sulfonic acids.

III. Electron Microscope Studies

IV. Emulsification of Silicone Rubber

   A. General survey of emulsifying techniques.

   B. General survey of commercially available wetting agents

   C. Synthesis of special wetting agents.

V. Removal of Volatile Oils from Gum

   A. Solvent extraction

   B. Molecular distillation

   C. Other techniques.

VI. Cross-Linkage in Silicone Rubbers

   A. Activators for benzoyl peroxide

      1. Substances forming free radicals

      2. Oxidizing compounds

      3. Accelerators from paint and plastics fields.

   B. Oxidation techniques

      1. Surface active metals

      2. Air Oxidation

      3. Other oxidation methods

   C. Lithium compounds

   D. Other Methods

I. STUDIES OF PIGMENTS

This portion of the program, which has already received considerable attention, is concerned with a continuing search for better pigments and for improved methods of altering the nature of the pigment-rubber interface. As received pigments are first tested (A) by compounding with silicone gum, using a 25-volume loading as a standard and using 2% benzoyl peroxide on the gum. The pigments which appear to be most promising in this preliminary test are pretreated in various ways (as by heating to remove adsorbed materials, coating with silicone films, etc.), and again compounded in 25-volume loadings (B) to determine whether pretreatment is beneficial. The pigments may also be compounded in variable loadings (C) to determine the optimum, or they may be compounded as mixtures of pigments (D). Milling techniques (E) receive attention at all times in an effort to improve this step.

A specific suggestion for altering the nature of the pigment-rubber interface has been offered by Dr. C.C. Vogt. This is concerned with the nature of the electrostatic charges on gum and pigment, a factor which is believed to be of importance in dealing with hydrocarbon rubbers. Plans are being made to include studies of electrostatic charges in future work.

A. Pigments As Received, 25-Volume Loading

A number of additional pigments have been studied as possible reinforcing agents. All of these pigments have been compounded at a 25-volume loading, using 2% benzoyl peroxide on the gum, as a means of preliminary evaluation. The pigments receiving attention during this period consist of a number of diatomaceous earths, some very finely-divided anatase titanias, several carbon blacks and a few miscellaneous choices. The results of these tests (Table I and Figure 1) and the properties of the pigments (Table Ia) show no particular correlation. In general, it will be seen that none of the pigments impart outstanding physical properties to the stocks, the tensile values lying in the range of 40 to 290 lb. per sq. in. There appears to be no correlation between mechanical properties and such factors as surface area, particle sizé and pH.

These data, together with data on numerous pigments included in our previous reports, cover about 50 pigments of widely varying nature as regards chemical constitution, particle size, particle shape, surface area and pH. The fact that the mechanical properties do not correlate with any of these factors points out clearly the necessity for further studies. These studies probably should not be aimed at extending the range of types of pigments, since a good variety has already been included. The emphasis should be aimed rather at an attempt to determine why the reinforcing effect varies so enormously for different pigments. It may be noted that the variation in tensile strengths for pigments studied to date is about 10-fold, indicating even greater specific effects of the pigment than those encountered in hydrocarbon rubber compounding. Unless the controlling factor(s) can be outlined it appears doubtful that pigments which yield stocks with tensile values above 400 lb. per sq. in. at the 25-volume loading will be found. Two techniques which will be of particular interest in the work to follow are the study of electrostatic charges and the application of the electron microscope.

TABLE I

Studies of As-Received Pigments at 25-Volume Loading

Pigment	Compound No.	Gms. pigment per 100 g.gum	Hardness	Tensile	Elong.
Silene EF	1099	57.0	41	145	156
Dicalite UF	1211	58.1	35	140	150
			35	242	162
			44	136	137
			38	141	162
			47	181	162
			42	168	187
			37	216	125
			48	187	125
Dicalite SA-3	1212	62.8	58	268	125
			46	216	137
AZO-ZZZ-66	1213	149.0	35	91	137
			40	108	137
Mapico Red. 387	1214	148.1	35	82	112
			34	88	125
Mapico Red 347	1215	148.1	48	139	125
			47	156	100
Mapico Tan 20	1216	120.0	50	190	150
			48	199	125
			45	173	175
			44	128	137
Furnex	1326	49.0	37	39	50
Sterling L	1327	49.0	No Cure		
Statex A	1328	49.0	40	178	150
			40	132	112
Statex B	1329	49.0	42	71	100
MP-561-1 Anatase TiO_2	1331	102.3	40	132	125
			43	147	125
MP-561-2 Anatase TiO_2	1332	102.3	42	144	137
			45	184	162
MP-561-3 Anatase TiO_2	1333	102.3	55	110	50
Santocel C	1363	55.0	65	220	62
			66	205	50
Santocel CX	1364	55.0	68	275	62
			68	293	62
Celite Snow Floss	1373	54.5	43	168	125
			42	163	125
Celite Super Floss	1374	62.5	40	179	125
			40	184	125

Table I-a

Properties of Pigments Tested

Pigment	Composition	Supplier	Specific Gravity	Surface Area sqm/gm	Particle Size Microns	pH
Silene EF	Hydrated ppt. calcium silicate	Columbia Chem. Div. Pittsburgh Plate Glass	2.10		0.2-0.3	10.0
Dicalite UF	Calcined diatomaceous silica	Dicalite Co.	2.15		2-40	7.5
Dicalite SA-3	Uncalcined " "	"	2.32		2-40	7.5
AZO-ZZZ-66	French process lead free zinc oxide	American Zinc Sales Company	5.6			0.1
Mapico Red 387	99.3% Fe_2O_3	Binney & Smith	5.18		0.06	6-8
" " 347	" "	"	5.18		0.06	6-6.5
" Tan 20		"	4.40		0.1-0.8	9-9.8
Furnex	SRF Black	"	1.8	36		9
Sterling L	HMF "	G. L. Cabot	1.8	34	0.06	9
Statex A	CF "	Binney & Smith	1.8	72		9
Statex B	FF "	"	1.8	72		9
MP-561-1	Anatase TiO_2	National Lead Co.	3.86		0.06-0.3	
MP-561-2	"	Titanium	3.86		0.01-0.12	
MP-561-3	"	Division	3.86		0.01-0.06	
Santocel C	SiO_2 89.5-91.5% Na_2SO_4 2.5-3.5%	Monsanto Chem. Co.	2.2		3-5	3.5-4

Table I-a (Cont.)
Properties of Pigments Tested

Pigment	Composition	Supplier	Specific Gravity	Surface Area sqm/gm	Particle Size Microns	pH
Santocel CX	Al_2O_3 & Fe_2O_3 1% Volatile 5-6%	Monsanto Chem.Co.	2.2			3.5-4
Celite Snow Floss	Uncalcined Diatomaceous silica	Johns-Manville	2.0		1-2	
Celite Super Floss	Flux Calcined " "	"	2.3		2-4	

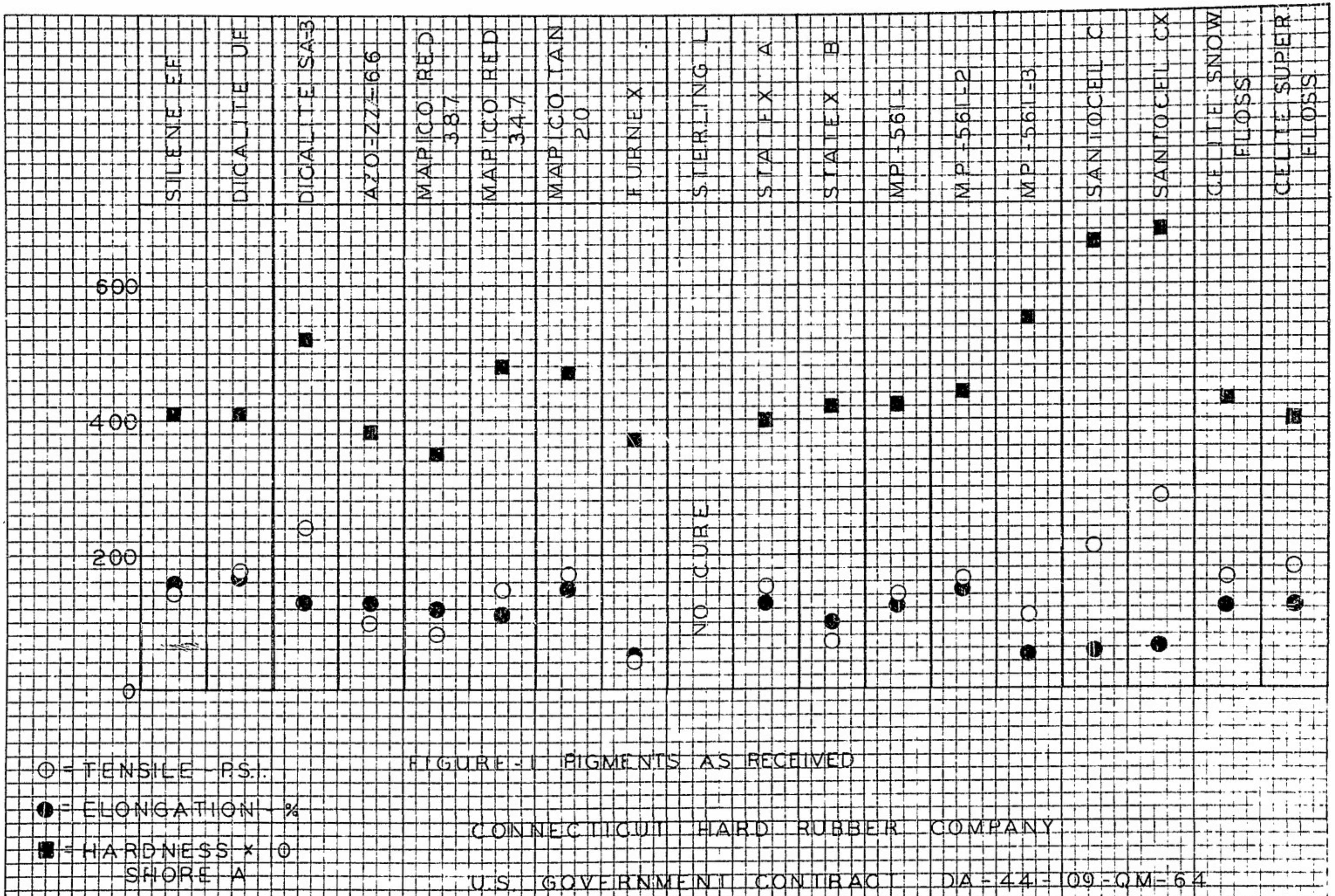

FIGURE - 1 PIGMENTS AS RECEIVED

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C. Pigments As-Received or Pretreated, Variable Volume Loadings

The preliminary evaluation of pigments at the 25-volume loading is used in this program simply to serve as an indication as to which pigments should be evaluated more thoroughly. The present data are concerned with three pigments which showed promise at the 25-volume loading (see Final Progress Report on Contract W-44-109-qm-2161). The pigments are Super-Multiflex (precipitated calcium carbonate). Silene EF (calcium silicate, 0.2-0.3 micron) and Rayox 110 (A rutile titanium dioxide). In general, the tensile strength increases with larger volume loadings at first, passes through a maximum and then decreases. The hardness increases steadily with an accompanying decrease in elongation.

Specifically, as shown in Table II and Figure 2, the stocks compounded with Super-Multiflex showed a steady increase in tensile strength and hardness up to a 40-volume loading. Stocks with higher loadings than this did not cure properly. The physical properties at the highest loading were: tensile, 200; elongatinn, 325; hardness, 53. The stocks compounded with Silene EF showed a maximum tensile strength of 180 lb. per sq. in. at the 30-volume loading; the elongation was only about 100% at this point. Rayox 110 stocks were somewhat harder stocks with the following physical properties at the 54-volume loading which gave the highest tensile value: tensile, 280; elongation, 137 1/2; hardness, 63.

Thus none of the stocks compounded with these pigments are of interest. Further studies of this type are a necessary part of the continuing program.

TABLE II

Studies of As-Received Pigments at Variable Loading

Pigment	Cpd. No.	Vol. Pigment per 100 vol. gum	Wt. pigment per 100 wt. gum	Hard-ness	Tensile Strength	Elong-ation
Super Multiflex	1248	10	29	28	47	188
	1249	20	58	27	111	304
	1108	25	72	31	142	375
	1250	30	86	33	161	413
	1251	40	115	53	205	319
	1365	50	144	Poor Cure		
	1366	60	172	No Cure		
Silene EF	1252	10	23	26	52	256
	1253	20	46	40	114	181
	1099	25	57	41	145	156
	1254	30	68	47	180	125
	1255	40	91	52	134	75
Rayox 110	1244	11	45	30	61	169
	1245	22	91	37	105	175
	1118	25	105	39	98	179
	1246	32	137	39	154	163
	1247	43	182	45	243	210
	1369	54	228	63	284	131
	1368	65	274	63	197	94

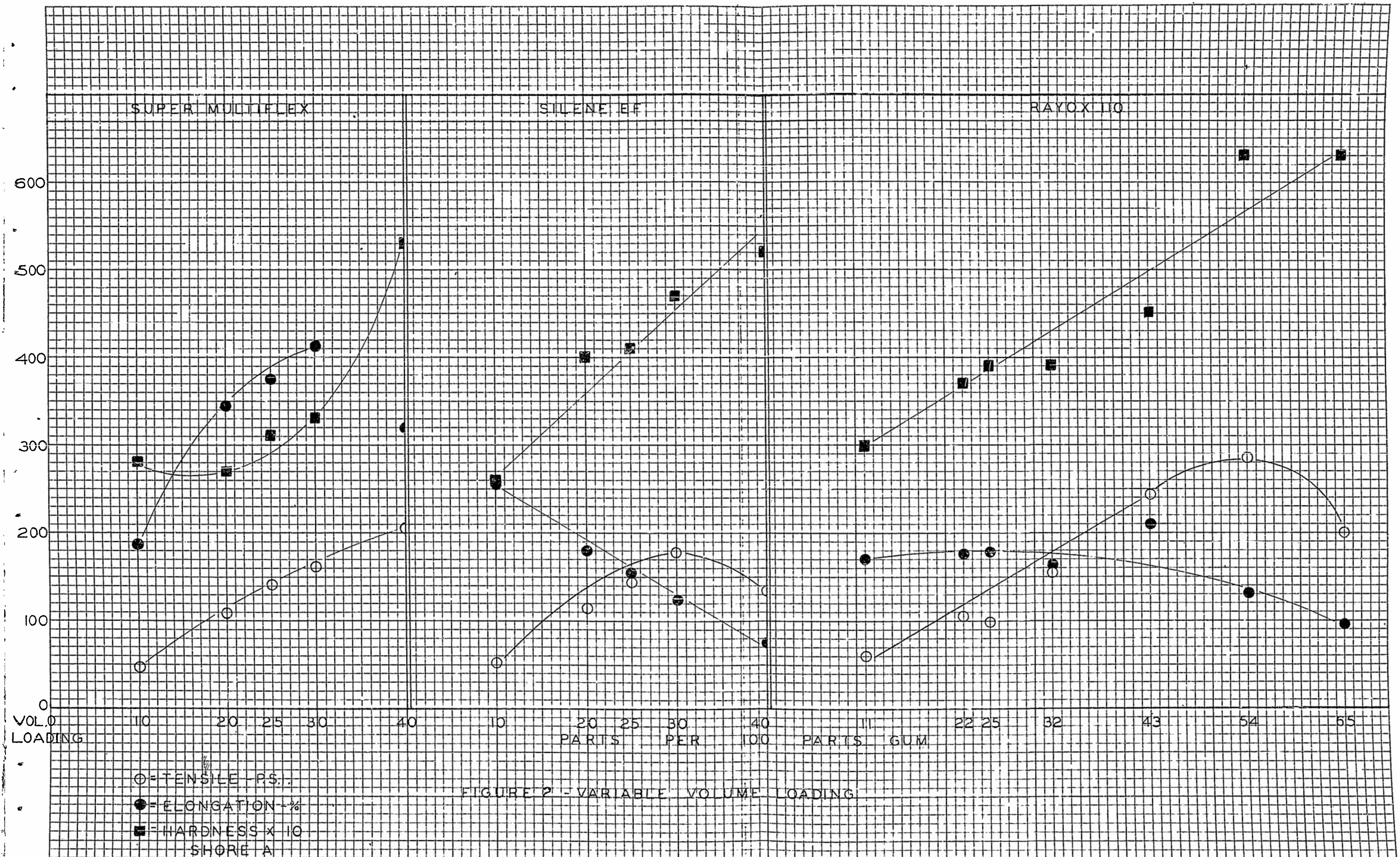

FIGURE 2 - VARIABLE VOLUME LOADING

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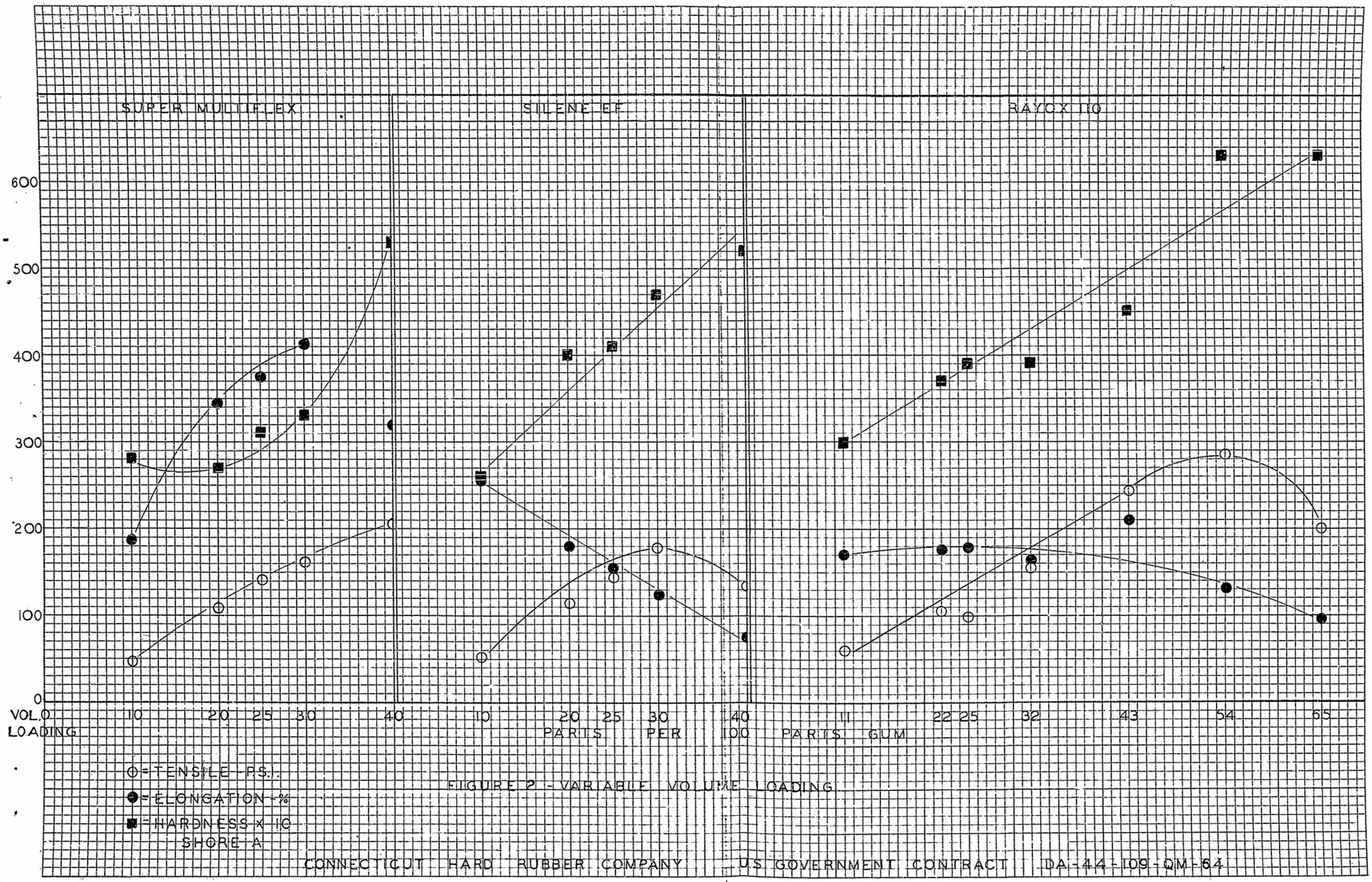

FIGURE 2 - VARIABLE VOLUME LOADING

D. Mixtures of Pigments

A study of pigment mixtures as reinforcing agents for silicone rubber was prompted by the possibility that stocks containing such mixtures might combine the desirable properties imparted by each pigment. For example, Prolox 166 yields relatively soft stocks with low tensile values whereas Alon yields harder stocks with higher tensile values. Unless the properties imparted to the stock are simply additive, there exists the possibility of preparing a stock with the mixture of pigments which would retain the higher tensile strength characterizing Alon and the softness of Protox 166. Furthermore, even if the properties are simply additive the combination of pigments permits the preparation of stocks with specific properties. This can be accomplished in using single pigments most easily by altering the volume loading. Thus the technique simply adds another degree of freedom in compounding practice.

Data on the following mixtures of pigments are reported in Table III and in Figures 3 and 4.

Alon - Celite 505

Hi-Sil-Celite 505

Protox-166-Celite 505

Rayox 110-Celite 505

Micromex W-6-Celite 505

Protox-166-Alon

Protox-166-Hi-Sil

Super-Multiflex-Celite 505.

The total loading in all cases except the Micronex-Celite mixture was arbitrarily held constant at 100 parts by weight of total pigments to 100 parts of gum. In the exception noted the loading was maintained at 75 parts by weight of total pigment . Benzoyl peroxide equivalent to

2 parts per 100 parts gum was used in all cases.

Inspection of the data reveals that the properties imparted by the pigments are essentially linear in the proportions of the two pigments. The technique may prove useful in later work but its further application probably should be delayed until more favorable results are obtained in the preliminary evaluation of pigments or in the curing step.

TABLE III

Pigment Mixtures for Reinforcing Silicone Rubber

Weight loading of Pigments parts per 100 parts gum		Volume loading of Pigments Vol. per 100 vol. gum		Compound No.	Hardness	Tensile Strength	Elong-ation
Alon	Celite 505	Alon	Celite 505				
0	100	0	43	1196	57	388	104
25	75	6	32	1189	51	308	138
33	67	8	29	1198	52	289	148
50	50	13	21	1190	53	291	147
67	33	17	14	1197	54	265	155
75	25	19	11	1191	57	330	175
98	0	25	0	1121	55	307	228
Protox 166	Celite 505	Protox 166	Celite 505				
0	100	0	43	1196	57	388	104
25	75	4	32	1227	51	272	163
33	67	6	29	1228	53	310	153
50	50	8	21	1229	43	230	228
67	33	11	14	1230	41	173	244
75	25	13	11	1231	40	131	237
100	0	17	0	1062	38	91	181
Hi-Sil	Celite 505	Hi-Sil	Celite 505				
0	100	0	43	1196	57	388	104
25	75	12	32	1238	67	450	94
33	67	15	29	1237	72	343	63
50	50	23	21	1236	79	342	50
67	33	31	14	1235	91	Too Brittle	
75	25	35	11	1234	92	Too Brittle	

TABLE III continued

Rayox 110	Celite 505	Rayox 110	Celite 505	Compound No.	Hardness	Tensile Strength	Elong-ation
0	100	0	43	1196	57	388	104
25	75	6	32	1243	48	415	169
33	67	8	29	1242	48	375	150
50	50	12	21	1241	46	327	150
67	33	16	14	1240	42	224	150
75	25	18	11	1239	41	203	175
100	0	24	0	1361	38	125	156
Micronex W-6	Celite 505	Micronex W-6	Celite 505				
0	75	0	32	1362	45	204	106
15	60	8	26	1263	62	243	88
30	45	15	19	1264	75	296	44
45	30	23	13	1265	84	391	38
50	25	25	11	1266	No Cure		
Protox 166	Hi-Sil	Protox 166	Hi-Sil				
25	75	4	35	1281	No Cure		
33	67	6	31	1282	No Cure		
50	50	8	23	1283	69	262	56
67	33	11	15	1284	61	266	81
75	25	13	12	1285	52	197	81
100	0	17	0	1062	38	91	181
Protox 166	Alon	Protox 166	Alon				
0	98	0	25	1121	55	307	228
25	75	4	19	1286	40	263	256
33	67	6	17	1287	46	311	250
50	50	8	13	1288	25	159	275
67	33	11	8	1289	26	156	306

Protox 166	Alon	Protox 166	Alon	Compound No.	Hardness	Tensile Strength	Elong-ation
75	25	13	6	1290	22	84	263
100	0	17	0	1062	38	91	181
Super Multiflex	Celite 505	Super Multiflex	Celite 505				
0	100	0	43	1196	57	388	104
25	75	9	32	1351	60	247	75
38	62	13	29	1350	59	275	94
50	50	17	21	1349	57	239	100
63	38	22	16	1348	48	225	125
75	25	26	11	1347	51	234	131
100	0	35	0	1352	48	138	138

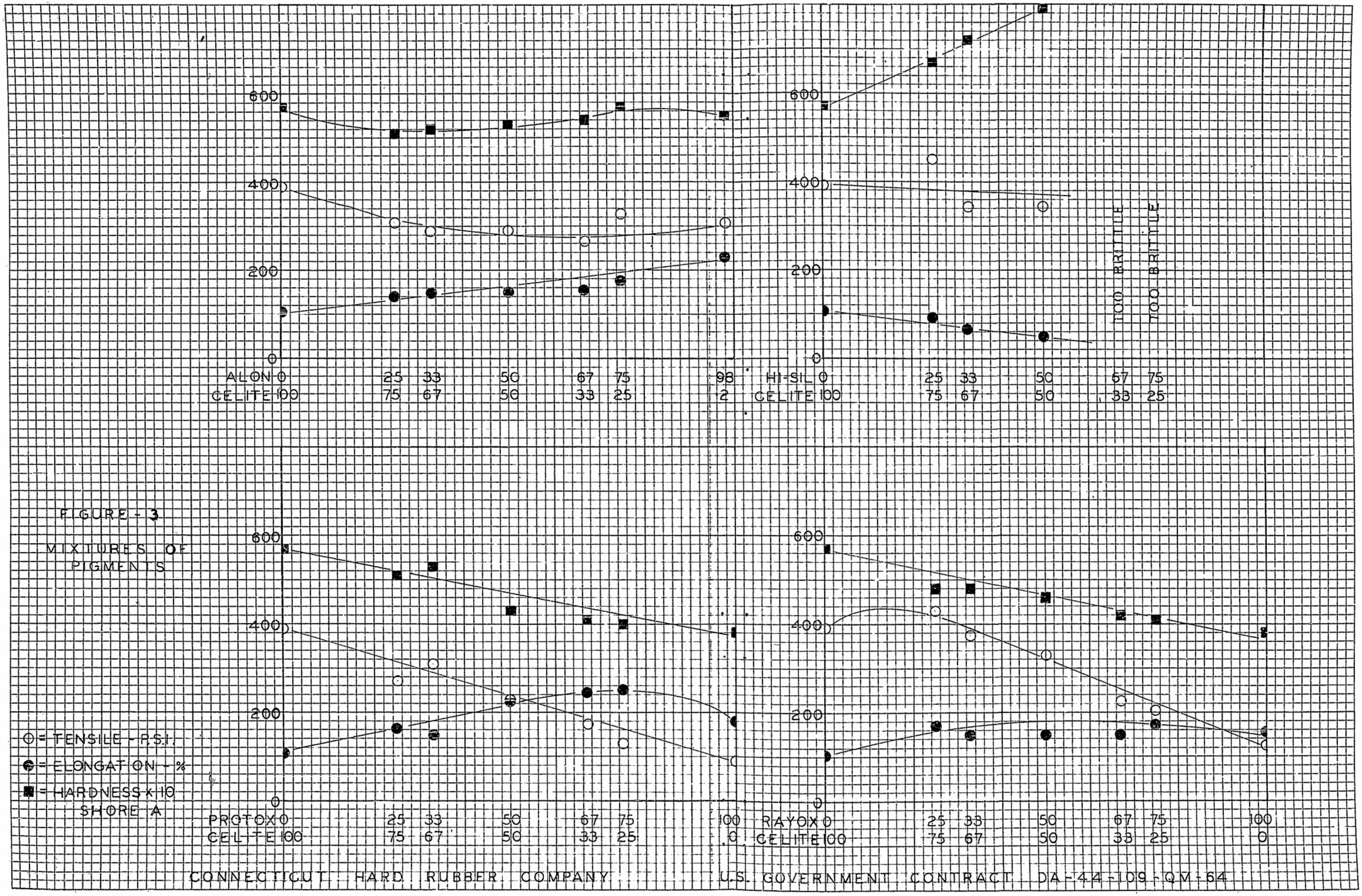

FIGURE - 3
MIXTURES OF PIGMENTS
O = TENSILE - P.S.I.
● = ELONGATION - %
■ = HARDNESS x 10 SHORE A
600
400
200
0
ALON 0 25 33 50 67 75 98
CELITE 100 75 67 50 33 25 2
HI-SIL 0 25 33 50 67 75
CELITE 100 75 67 50 33 25
100 BRITTLE
100 BRITTLE
PROTOX 0 25 33 50 67 75 100
CELITE 100 75 67 50 33 25 0
RAYOX 0 25 33 50 67 75 100
CELITE 100 75 67 50 33 25 0
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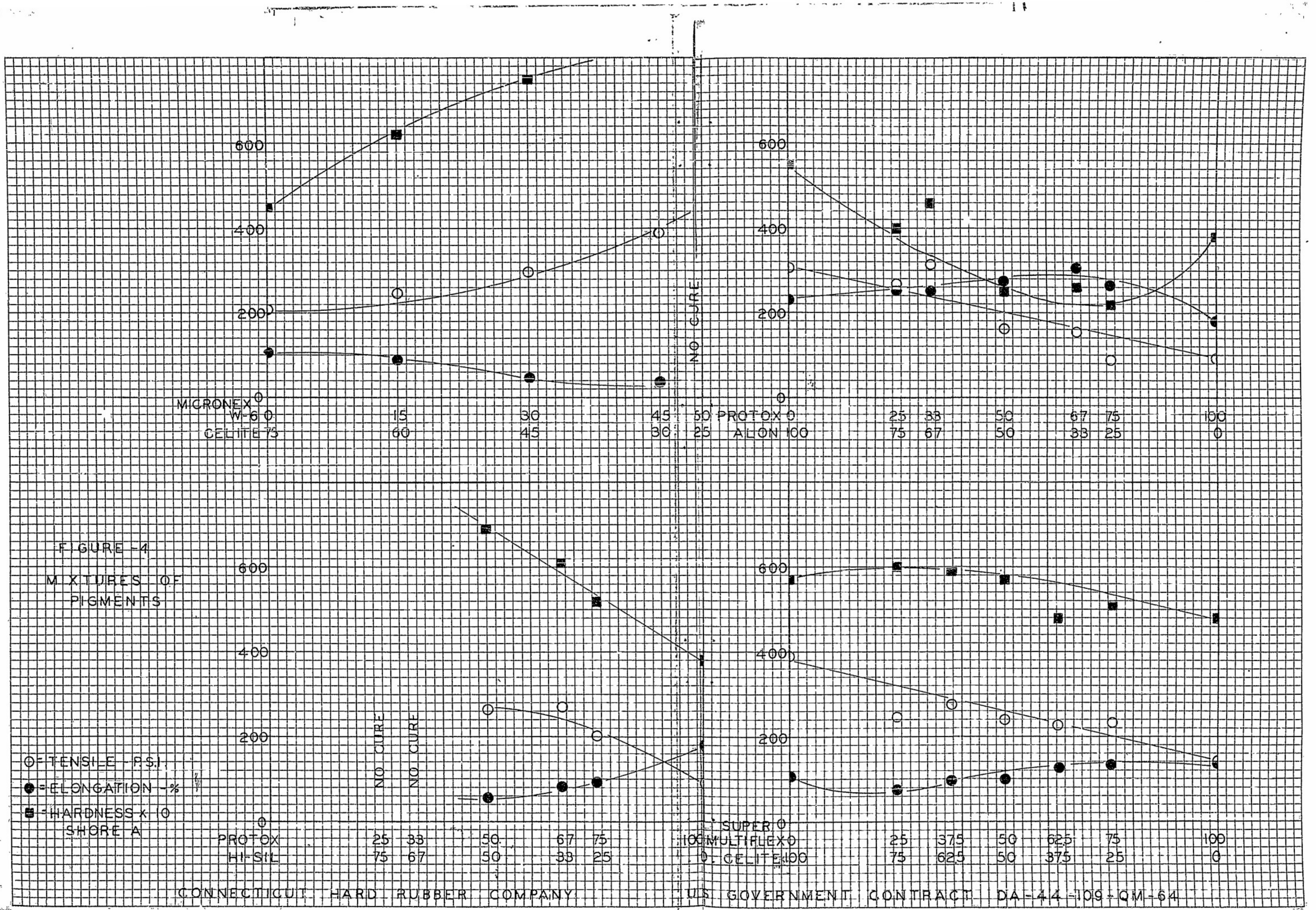

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E. Milling Techniques

The lack of reproducibility of the physical properties of similar batches of silicone stock led to a study of the causes of this difficulty sinse a knowledge of the probable error in physical properties is necessary in interpreting results. Such lack of reproducibility might result from differences in the raw materials used, from variations in the milling technique or from the methods of testing. To permit an evaluation of the distribution of results a particular stock was chosen to be compounded as a control mixture by the technicians at least once every working day for a period covering about 2 1/2 months. The particular mixture chosen consisted of 100 parts by weight of gum (G.E. 9979-G), 58 parts by weight of Celite 505 and 2 parts of benzoyl peroxide. A total of 106 batches of this stock have been prepared and tested with the results shown in Figure 5. The results have been analyzed by statistical methods:

	Minimum Value	Maximum Value	Mean Value	Probable error	Deviation for 4/5	Deviation for 9/10
Hardness	31	59	43	4	7	9
Tensile	50	360	203	36	69	89
Elongation	62	275	132	24	46	60

The terms used in this table are defined as follows:

Mean Value: Simple arithmetic average of 106 tests

Probable error: The probability is 0.50 that the true value of the property lies within the range of the mean value value plus or minus the probable error.

Deviation for 4/5: The probability is 0.8 that the true value of property lies within the range of the mean value plus or minus this quantity.

Deviation for 9/10: Same as above, except probability is 0.9

The scattering of rosults is seen to be so great that the probable error of the mean of 106 tests is about 10%, representing a very low degree of precision. It is believed that differences in the properties of the raw materials are not of great importance, since considerable disagreement has been noted in the physical properties of batches milled within an hour of each other by the same technician using the same raw materials. Furthermore, there is no correlation of results on a time basis as would be expected when a change in the nature of the gum or Celite occurred (as by aging, moisture content, etc.) if the discrepancies were due to variations in the raw materials. Variations in the milling technique have been maintained as low as possible by standardizing the order of putting the materials on the rolls and the time of milling. That there are some variations in the results produced by the milling is well established, however, because it is known that the entire variation is not due to the testing methods, the remaining possibility. Another check on milling technique is discussed below. Methods of testing are not entirely satisfactory since the Scott tester is being used in a very low range of tensile values. In this range as error of even 1/4 lb. in the reading at break can lead to a relatively large percentage error.

As a further check on the milling technique, samples of gum and pigments from this laboratory were milled on an 8" x 16" laboratory mill in the General Electric Co. plant. The mill used was a new one, equipped with independent variable-speed drives on the rolls, 2% benzoyl peroxide on the gum was used in all cases. The curing cycle was: 15 hr. at 212°F., 4 hr. at 302°F., 67 hr. at 392°F. The results are tabulated below:

Pigment & loading	Compound No.	Milled	Remilled	Press-cured	Oven-cured	Tensile	Elongation	Hardness
Celite 505 (150)	1169	G.E.		G.E.	C.H.R.	745	50	84
		G.E.	C.H.R.	C.H.R.	C.H.R.	705	50	86

Pigment & loading	Compound No.	Milled	Remilled	Press-Cured	Oven-cured	Ten-sile	Elong-ation	Hard-ness
Celite 505 (150)	1169	G.E.		C.H.R.	C.H.R.	630	50	85
		C.H.R.		C.H.R.	C.H.R.	692	75	79
Celite 505 (100) plus R-510 TiO_2 (75)	1056	G.E.		G.E.	C.H.R.	860	58	84
		G.E.	C.H.R.	C.H.R.	C.H.R.	862	67	85
		G.E.		C.H.R.	C.H.R.	825	58	84
		C.H.R.		C.H.R.	C.H.R.	666	67	80

It will be noted that results obtained with the Celite batch are reasonably consistent; i.e., the batch milled at Connecticut Hard Rubber Co. gave essentially the same properties as the batch milled at General Electric. This might be expected in view of the fact that this batch is easy to compound because the gum seems to wet the Celite without difficulty.

Results obtained with the Celite-TiO_2 batch, which is a dry mix in that the gum wets the pigment only with difficulty, are not so consistent. The tensile value obtained on a batch compounded at Connecticut Hard Rubber Co. is about 20% below that resulting on a batch compounded at General Electric. Whether this difference is really significant is not possible to judge from these data. Even if it is significant, the result indicates that no gross reduction in tensile properties is produced by the milling technique in use. It may be concluded only that milling technique or the limitations of the mill being used may account for part of the discrepancy in physical properties but not all of it.

Returning now to a consideration of the results of the control tests represented by 106 batches, it will be noted that the tensile value of this batch is about one-fourth of the tensile value of the batches involved in the work at General Electric. It appears possible that milling technique and testing methods might be much more critical in such weak stocks than they are in stronger stocks. Thus the discrepancies may be much less serious in testing the latter. It is intended to run several batches of the Celite-titania mixture on the laboratory mill in the near future to determine whether this is correct.

The milling technique will be studied further within the next few weeks when a new 10" x 20" mill is installed in the plant of the Connecticut Hard Rubber Co. This is being installed as a production mill by the company but it is planned to use it also for mixing some of the batches in this program. A relatively small number (10-20) of Celite batches should be sufficient to permit determination of the extent to which milling is responsible for the lack of reproducibility. If the limitations of the small laboratory mill are an important factor in causing scattering of results it will be necessary to use the new mill in the future work of this program. Batches as small as one pound can be handled satisfactorily on this mill. Thus, by the time of the next report it should be possible to decide whether the lack of precision in results is due to milling techniques or to testing methods or to both.

Finally, it should be noted that the lack of precision in these control tests has little effect on the major conclusions reached to date in this program. This is true in part because the compounding program so far has served primarily to indicate that (a) there is a marked specificity in the reinforcing effect of various pigments and (b) the problem of improving the physical properties of silicone rubber stocks apparently can be solved only in part by the compounding. In other words, this portion of the program might be considered to be unsuccessful in that it has not yielded any stocks of greatly improved characteristics but it has been quite successful in pointing out that we must try to determine the reason for the specific effects of the various pigments and that other methods of improving the stocks (such as curing methods) must receive a great deal of attention. These factors are emphasized by the data even though they may be of low precision. It may also be noted that data on such factors as pigment mixtures, effect of peroxide concentration, etc, show considerably more consistency than would be expected if the scattering of data were as marked as is the case with the control batches, indicating the possibility that the particular mixture chosen for the control batch is unusually sensitive to the effect of some undetermined variable.

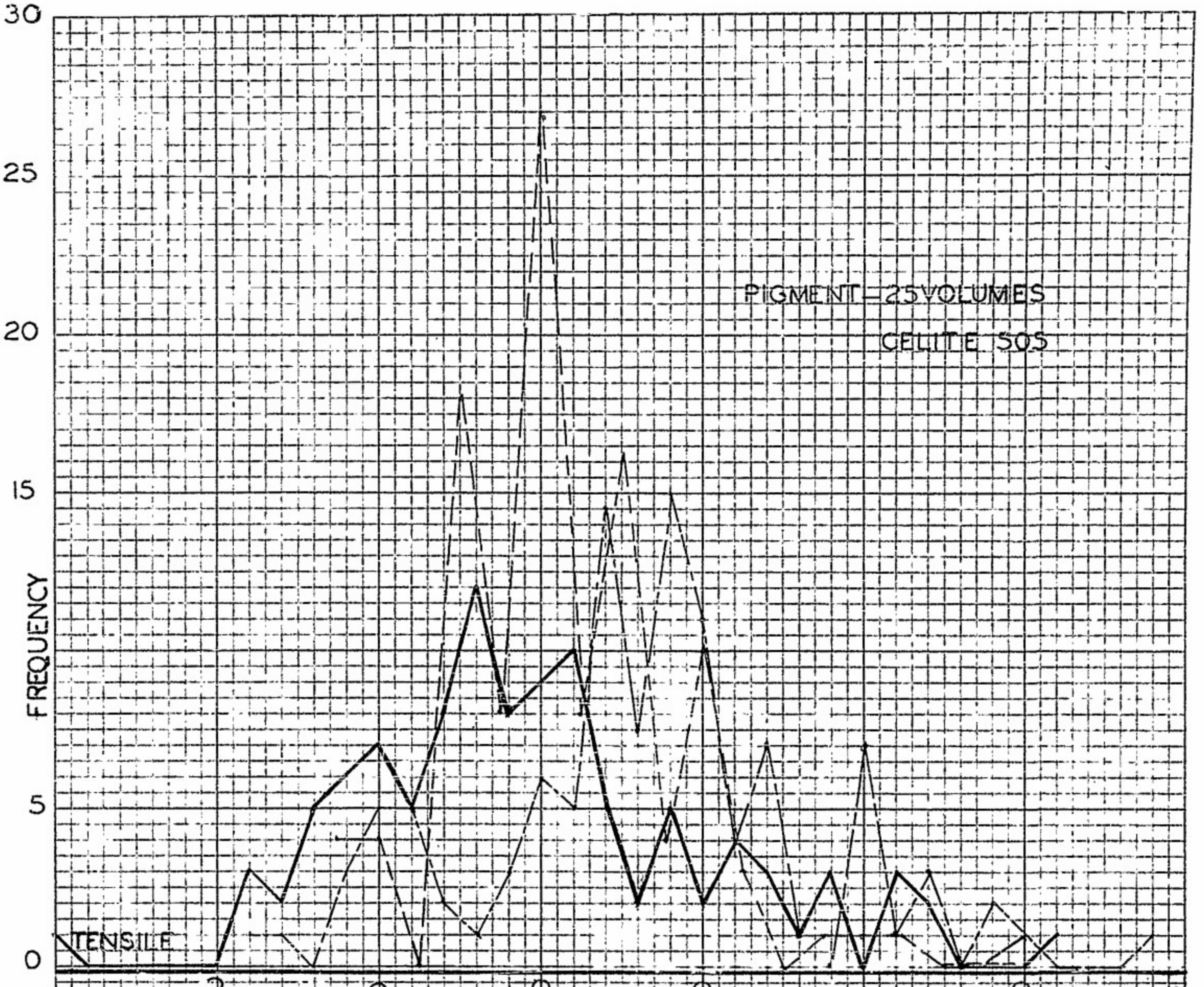


FIGURE - 5

DISTRIBUTION OF PHYSICAL TEST RESULTS

CONNECTICUT HARD RUBBER COMPANY

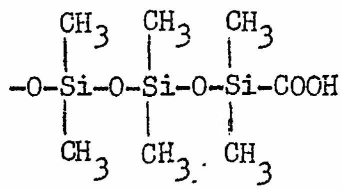
US GOVERNMENT CONTRACT DA-44-109-QM-64

II. WETTING AGENTS FOR PIGMENT-RUBBER SYSTEMS

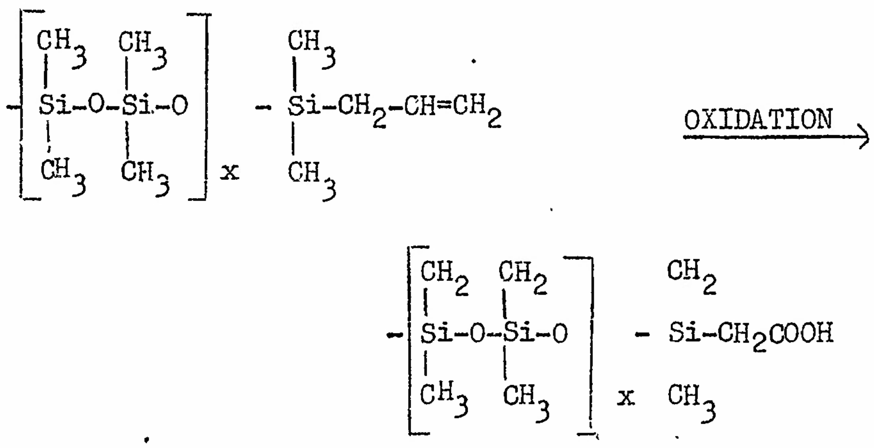
The nature of the pigment-rubber interface is most easily modified by changing the nature of the pigment surface by methods previously noted. Another definite possibility is the addition to the pigment-rubber system of a material which would be strongly adsorbed on the pigment and which would be compatible with the gum. Such a material is available in stearic acid for hydrocarbon rubber systems. In dealing with silicone rubbers it is assumed that it will be necessary to provide a molecule which will be strongly adsorbed by the pigment and which will have a chain compatible with the gum. Aliphatic carboxylic acids have been tried in this laboratory but they do not show the marked effect which stearic acid shows in hydrocarbon rubbers. Other commercially available materials have been tried and may be tried in the future. A more promising attack would appear to lie in the synthesis of silicone carboxylic acids or silicone sulfonic acids, in which the acid group might provide for strong adsorption while the rest of the molecule would be miscible with the gum.

p-Trimethylsilylbenzoic acid has been synthesized in this laboratory by use of the Grignard reaction, as described later in this report. Results obtained on using this material as a possible wetting agent in a batch containing a 25-volume loading of Celite 505 and in a batch containing 75 parts by weight of TiO_2 and 100 parts by weight of Celite 505 are given in Table IV and Figure 6. 2% benzoyl peroxide on the gum was used in all these batches. The silicone acid has essentially no effect on the physical properties of the stocks in concentrations up to 3 parts by weight of the acid to 100 parts of gum. The technician reported that the pigments were incorporated somewhat more easily in the gum in these batches.

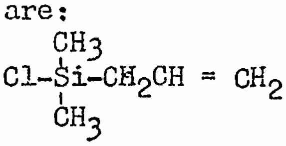
The benzoic acid derivative described above was synthesized largely as a matter of developing technique. It does not contain a silicone chain, which is assumed to be the most logical method of insuring compatibility with the gum. The type of structure which is desired is:

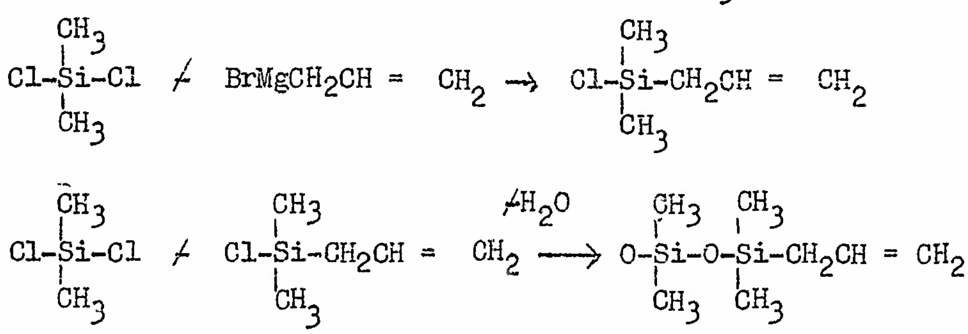


Methods of preparing such compounds now under investigation include the oxidation of the proper allyl compounds:

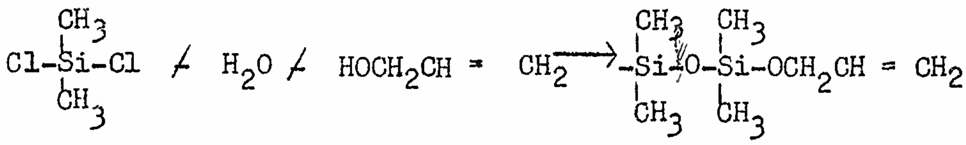


Possible methods of synthesizing the allyl compound are:

1. Cohyrolysis of mixtures of $(CH_3)_2SiCl_2$ and 



2. Simultaneous hydrolysis and alcoholysis of $(CH_3)_2SiCl_2$



Synthesis of p-Trimethylsilylbenzoic Acid (Experimental)

One hundred eighteen grams (.5 moles) of p-dibromobenzene were dissolved in 250 cc. dry ether by warming for a short time on a steam bath, and the solution was added slowly to 12.5 g. (a little more than .5 moles) magnesium turnings which had been covered with 100 cc. dry ether. The entire apparatus had previously been heated and swept out with nitrogen. A few crystals of iodine were added to catalyze the reaction. It was necessary to warm the reaction flask with a pan of hot water in order to start the reaction, but once started, it proceeded satisfactorily.

p-Bromotrimethylsilylbenzene

Fifty four grams (.5 moles) of chlorotrimethylsilane were dissolved in 50 cc ether and added slowly to the reaction flask containing the p-bromophenylmagnesium bromide. The solution was refluxed for 4 hours and allowed to stand overnight. The ether was evaporated and the resulting paste was heated for an hour at a temperature which did not cause appreciable fuming. The ether which had been distilled was returned to the flask, and water, acidified with a little HCl, was added to the milky suspension. The ether layer was shaken several times with water (ca. 500 cc in all) and separated. The ether contained a finely divided gummy solid which was filtered after the addition of a small quantity of supercel. The aqueous layer was shaken with ether (ca. 200 cc in all) and the extracts combined. The ether solution was dried over sodium sulfate and the ether removed.

The p-bromotrimethylsilylbenzene was dissolved in an equal volume of ether and added slowly to a well stirred mixture of 3.4 g. magnesium turnings and ether. After the addition of 5-10cc, the flask was warmed and a few crystals of iodine were added. The mixture was refluxed for an hour before the reaction began to take place. The remaining halide was added slowly and the refluxing continued for several hours until all the magnesium had reacted.

The clear solution containing the p-trimethylsilylmagnesiumbromide was filtered rapidly and poured on to an excess of crushed dry ice. A vigorous reaction took place. The mixture set to a pasty mass and was left in this condition overnight. The reaction flask was rinsed with 20 cc dry ether and the filtered washings were added to the CO_2 mixture.

Ten percent HCl was added to the ether solution of the acid and the two layers separated. The water layer was washed with ether and the ether was added to the main portion. The ether layer was washed with water and extracted with 10% sodium bicarbonate solution, in the cold, until there was no further reaction. The bicarbonate layer was washed with ether and acidified in the cold. An oil formed which solidified readily on cooling. This was filtered and dried.

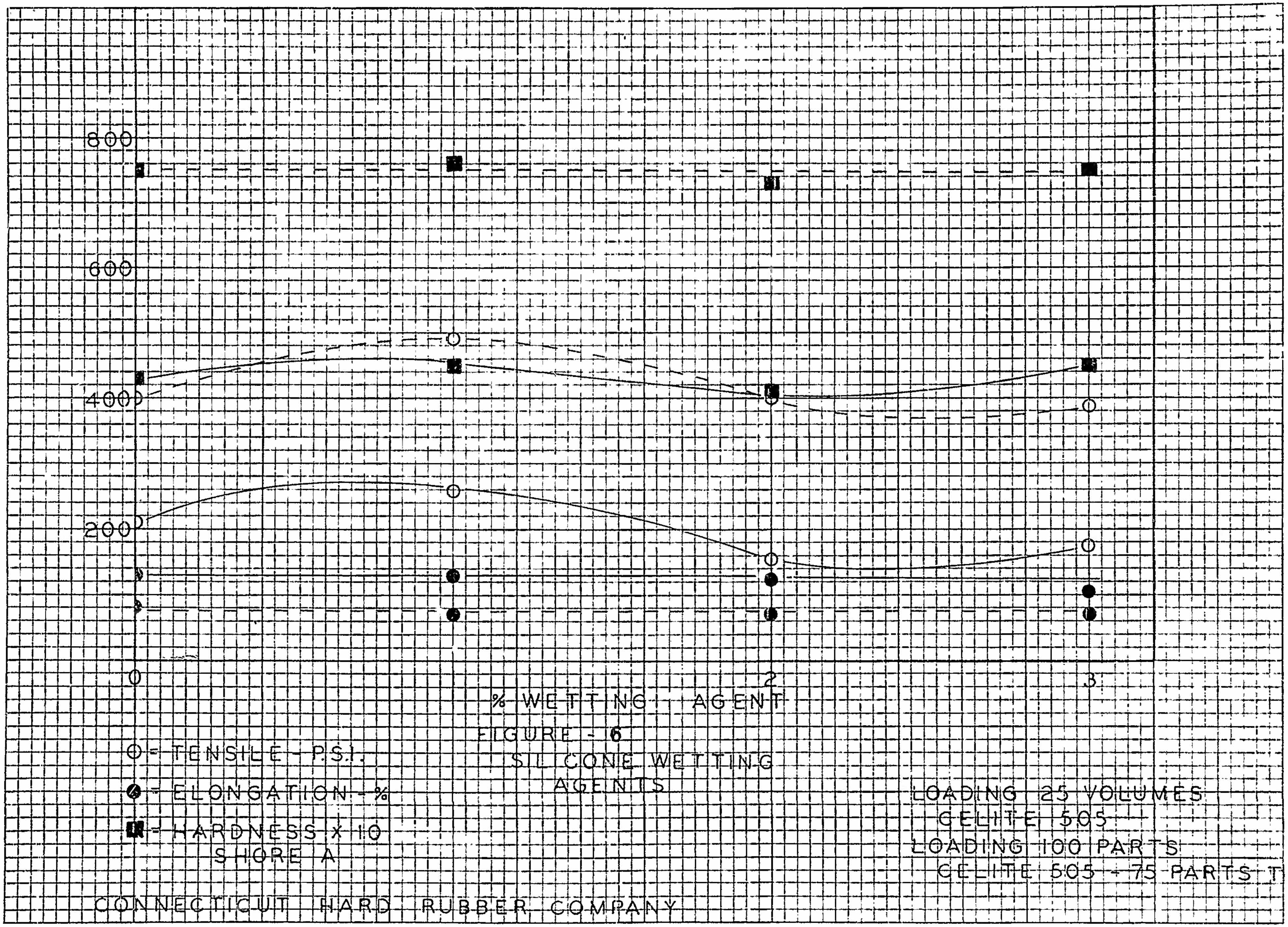
A sample of the acid (m.p. 108-110°) weighing .0802 g. was neutralized with 53.8 cc. of .00748 N NaOH. The neutral equivalent was thus 199.8. The theoretical value is 194.3.

Another sample was dried under vacuum for one week. .0184 g required 12.45 cc of .00748 N NaOH for neutralization. The neutral equivalent was 197.5.

TABLE IV

Use of p-Trimethylsilylbenzoic Acid
in Silicone Rubber Compounding

Pigment and Loading		Wetting Agent Concentration	Compound No.	Hardness	Tensile Strength	Elongation
Celite 505	25 vol.	0	1072	43	203	132
		1	1334	45	257	131
		2	1335	41	156	125
		3	1336	45	175	106
Celite 505	100 parts					
TiO_2	75 parts	0	1066	75	398	81
		1	1337	76	493	69
		2	1338	73	397	69
		3	1339	75	391	69



U.S. GOVERNMENT CONTRACT DA-44-109-QM-64

Preparation and Oxidation of Silicone Allyl Compound (Experimental)

In a preliminary evaluation of the possibilities of using the allyl compounds for synthesis, dimethyldichlorosilane (24.5g) was added dropwise to a well-stirred cooled solution consisting of a mixture of water (125 cc.), allyl alcohol (22 cc.) and sodium sulfate (15g.). Considerable heat was evolved during the reaction. The oil which separated was extracted with ether and the ether layer washed with a solution of sodium bicarbonate in water. The residual oil obtained by evaporation of the ether was oxidized by adding it to a solution of potassium permanganate (148g) and potassium hydroxide (16g.) in 1800cc. of water with rapid stirring. The reaction was slow. After warming for 1-2 hours and allowing to stand overnight the excess permanganate was destroyed by ethyl alcohol, the MnO_2 was filtered and the aqueous solution acidified. On extracting the aqueous solution with ether and evaporating, a small amount of silicon-containing solid was obtained. This solid is a carboxylic acid and is being characterized. Further work on this method of synthesis is in progress.

III. ELECTRON MICROSCOPE STUDIES

Objectives

In any fundamental study of silicone rubber and the mechanism of reinforcement, detailed information as to the size, shape and distribution of the pigments in the cured rubber is valuable if not essential. The electron microscope has extended the useful range of the optical microscope by a factor of nearly a hundred, making such a study possible even for the smallest size pigment particles.

The specific objectives of the program are as follows:

1- To obtain electron micrographs of each of the pigments used in the general study of silicone rubbers as qualitative and quantitative aid in the understanding of reinforcement or lack of it. The importance of particle size and area, for example, might be evaluated.

2- To obtain micrographs of specimens of cured rubber in order to observe the dispersion of the pigments and any other peculiarities which may give clues as to what determines the favorable or unfavorable properties. It is hoped that some information as to the size and nature of the macromolecules may be found with the development of suitable techniques.

Studies of this sort should serve to supplement and clarify the results of other experiments as well as to guide in the choice of new experiments.

Apparatus and Techniques

The Electron Microscope.

Due to the kind cooperation of Yale University and Dr. Mellnick of the Department of Preventive Medicine, arrangements were made to use the Yale R.C.A. Model EMU electron microscope in this program. Until recently this microscope was operated with no aperature in the objective lens, thus limiting the contrast and resolution of electron micrographs, especially for thick or dense specimens. We have now installed an objective aperature with marked improvement in pictorial results. Under skillful operation, this improved microscope should give pictures of comparable quality to any obtainable elsewhere.

Excellent descriptions of the R.C.A. microscope and its use are to be found in the two following books:

1- R.W.G. Wyckoff, ELECTRON MICROSCOPY, TECHNIQUE AND APPLICATIONS, Interscience Publishers, New York (1949).

2- Zworykin et al, ELECTRON OPTICS AND THE ELECTRON MICROSCOPE, John Wiley and Son, New York, (1945).

Pigment Studies

In order to obtain electron micrographs of individual particles, the pigment must be dispersed on or in a thin supporting film such as collodion. A transmission photograph is then obtained. The sparking technique of Ladd and Wiegand (Rubber Age, New York, 57, 299, 1945) was found to be simple and satisfactory. In this method, a thin film of collodion is cast on a water surface. A section of the film is then transferred to a glass slide by inserting the slide under the film and then removing it with the film attached. After drying, the slide is placed on a metal plate and a small amount of pigment scattered on top of the film. The pigment is then dispersed over the film by passing a Tesla Coil (vacuum leak tester) over the plate. The film is then floated off the slide onto a water surface and transferred to a 200 mesh, 1/8-inch diameter screen in the usual manner for electron microscope observation.

Cured Rubber Specimens

Electron micrographs of cured rubber can be obtained by directly photographing very thin specimens of the rubber or by photographing a thin replica of the surface of a fractured rubber specimen. Although both methods are to be used in the program, only the direct method has been tried so far. To obtain reliable information with this method, the films must not only be extremely thin (of the order of a few hundred angstrom units), but must be prepared in such a way as to insure the film being representative of the bulk rubber as normally prepared.

One obvious approach is to cut thin slices of the bulk rubber with a microtone. This is possible but difficult because of the very small thickness required (See W.A. Ladd and H.A. Brundle, RUBBER AGE 57, N. 6, 1945). Moreover, Ladd has compared the results of this method with those obtained by a simpler "Vulcanization Method" (W.A. Ladd INDUSTRIAL ENG. CHEMISTRY (ANAL. ED.) 16, 642, 1944), and has found no apparent discrepancies so we have chosen the latter technique for our first work with silicone rubber.

In this method, the uncured rubber is press cured into a very thin sheet between two 1/4" diameter aluminum discs subjected to pressures of the order of 50,000 to 200,000#/in.^{2}. One of the surfaces in contact with the rubber is convex, the other flat. Both are coated with a thin layer of collodion to provide a smooth surface and allow slippage of the rubber. The curing is done in a standard Carver press, three dish molds being spaced symmetrically between two 7" x 7" x 3/8" steel plates. Following the press cure and oven cure, the thin films are removed from the molds and the collodion by immersion in amyl acetate for about a week. The films are then placed on 200 mesh screens for electron microscope observation.

Pigments

Electron micrographs of most of the pigments have been obtained by using the sparking technique for dispersal and representative results are shown in plates 7-10. The magnification is indicated below each picture and a mark one micron long has been included in each print for comparison purposes.

The pictures obtained so far show in many cases, a grouping of the particles into aggregates. This may be and undoubtedly is, due to poor dispersion in many cases. Yet there is more evidence that a chain structure exists which has some permanence. This is particularly evident in Fume Silica where enlargements of the photographs show unmistakable bridges between particles. Ladd found such a "reticulate chain structure" in carbon blacks which persisted in the cured rubber. It will be interesting to see whether that situation exists for other pigments.

A quantitative statistical study of the particles sizes of these pigments has not yet been carried out but it is clear that this property alone cannot explain the reinforcing properties of the pigments. For example, the diatoms (Celite) and Alon differ in size by orders of magnitude and yet produce comparable silicone rubber stocks when used as a filler.

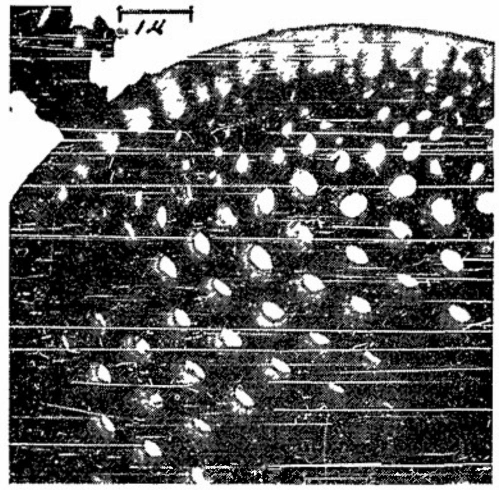
Cured Rubber

The technique of preparing and photographing cured rubber specimens is still in the development stage. In plate 11 are shown samples of an Alon loaded silicone rubber of the following composition:

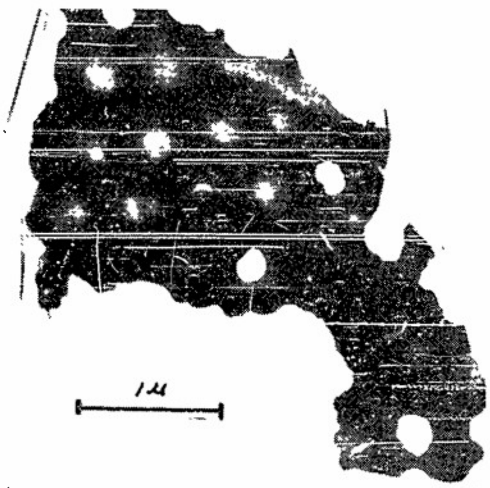
G.E. 9979-G gum	100
Benz. peroxide	2
Alon	98

This shows clearly the Alon particles dispersed in the fibrous tenacles of the rubber at the edge of torn piece.

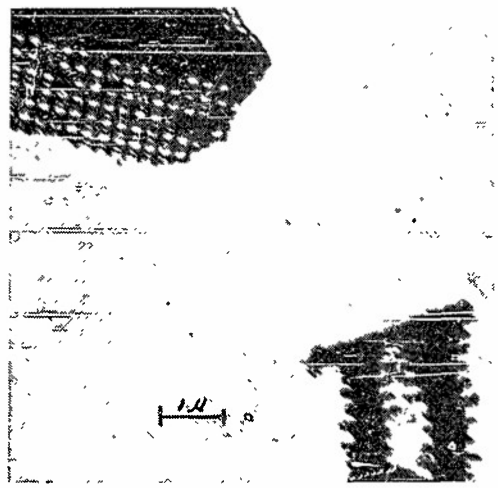
CELITE 505
9,700X



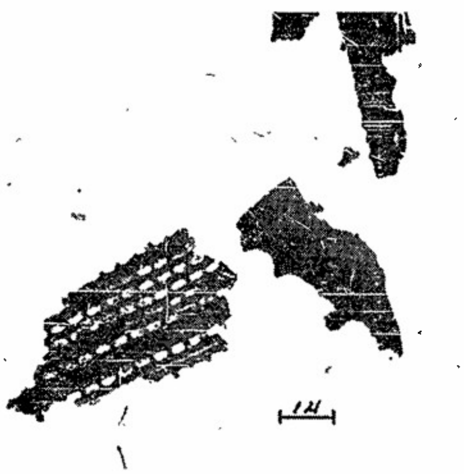
CELITE 505
8,300X



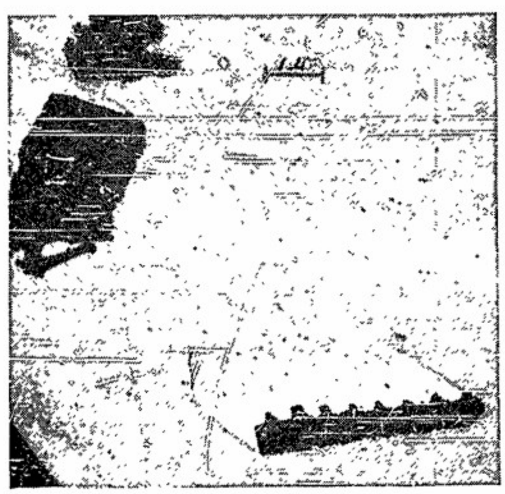
CELITE 505
19,400X



DICALITE WHITE
8,300X

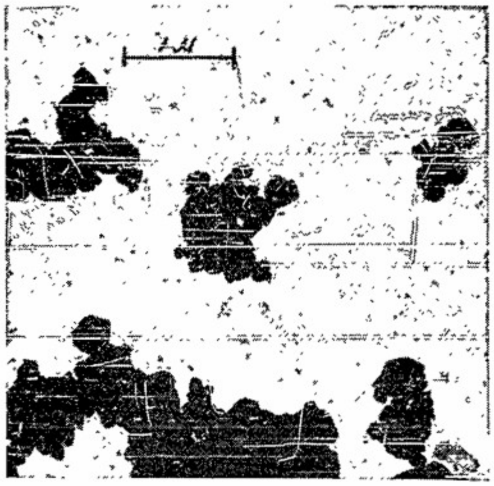


DICALITE PS
7,300X

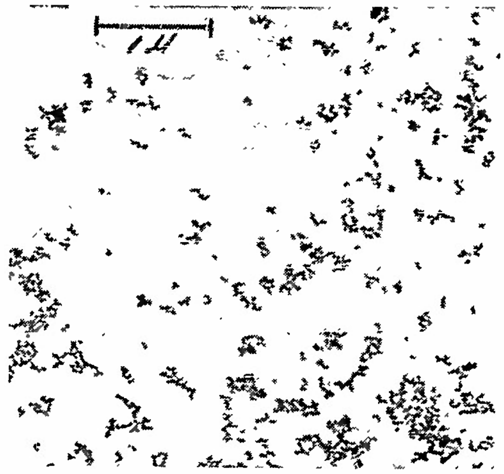


DICALITE PS
7,300X

PHOTOMICROGRAPHS OF VARIOUS PIGMENTS
PLATE 7

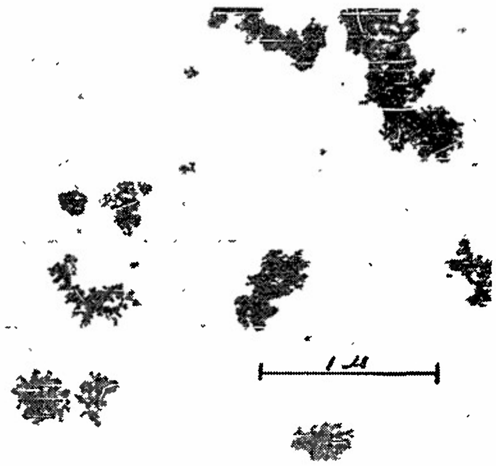


SILICA 1240
13,500X

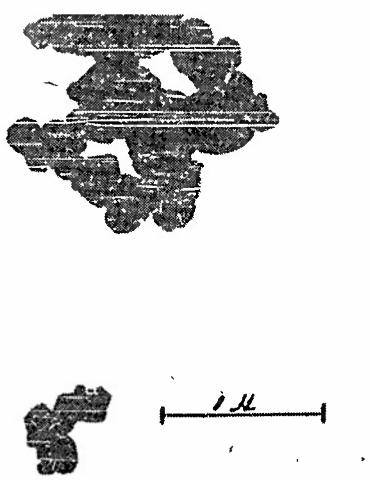


MICRONEX W-6
15,100X

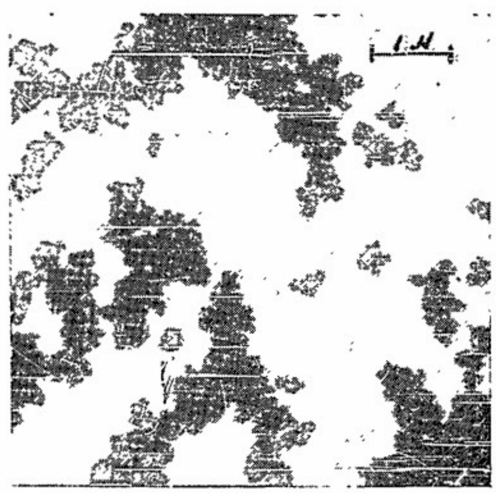
HI-SIL
26,800X



ALON
22,800X



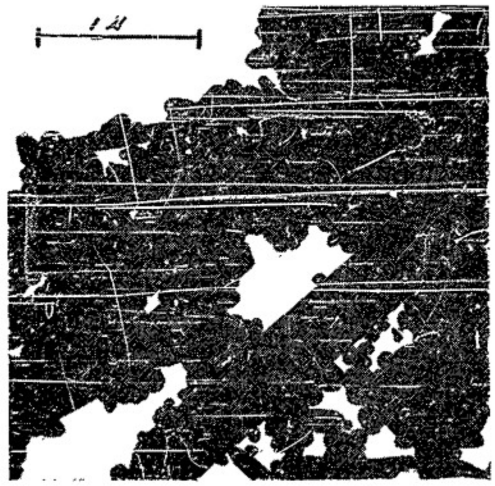
TITANIUM DIOXIDE
21,300X



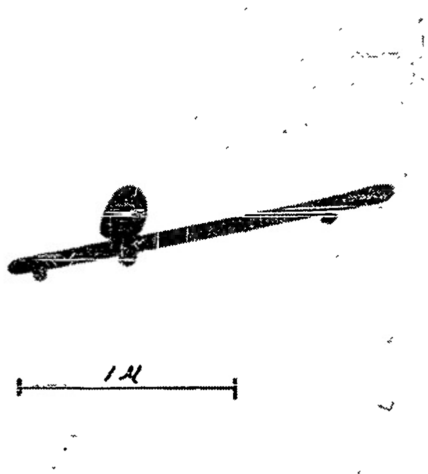
RAYOX 110
10,000X

PHOTOMICROGRAPHS OF VARIOUS PIGMENTS
PLATE 8

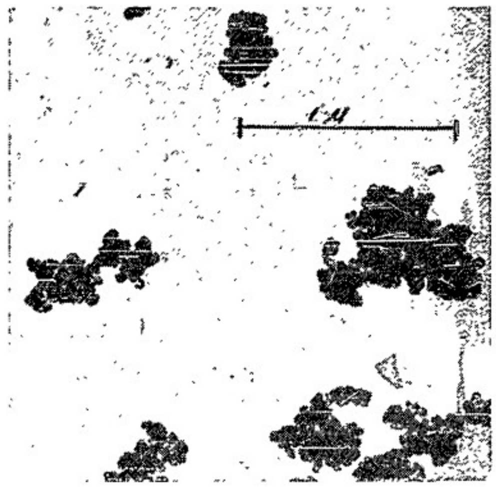
AZO-ZZZ-55
10,000X



AZO-ZZZ-55
21,300X



AZO-ZZZ-55
28,100X

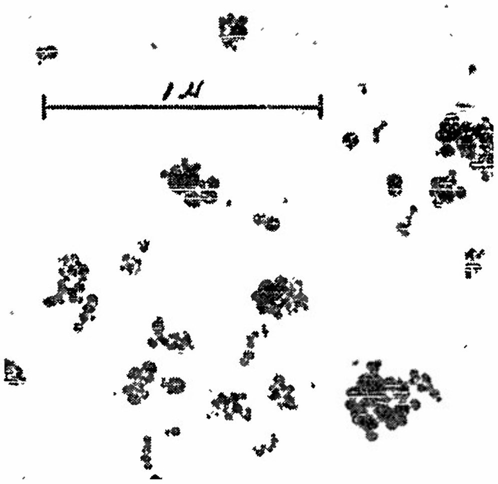


SUPER MULTIFLEX
28,100X

AZO-ZZZ-66
7,600X

AZO-ZZZ-66
10,000X

PHOTOMICROGRAPHS OF VARIOUS PIGMENTS
PLATE 9



FUME SILICA
34,800X

FUME SILICA
34,800X

MAPICO TAN 20
21,300X

MAPICO TAN 20
28,100X

RANEY NICKEL
13,500X

RUFERT NICKEL
8,300X

PHOTOMICROGRAPHS OF VARIOUS PIGMENTS
PLATE 10

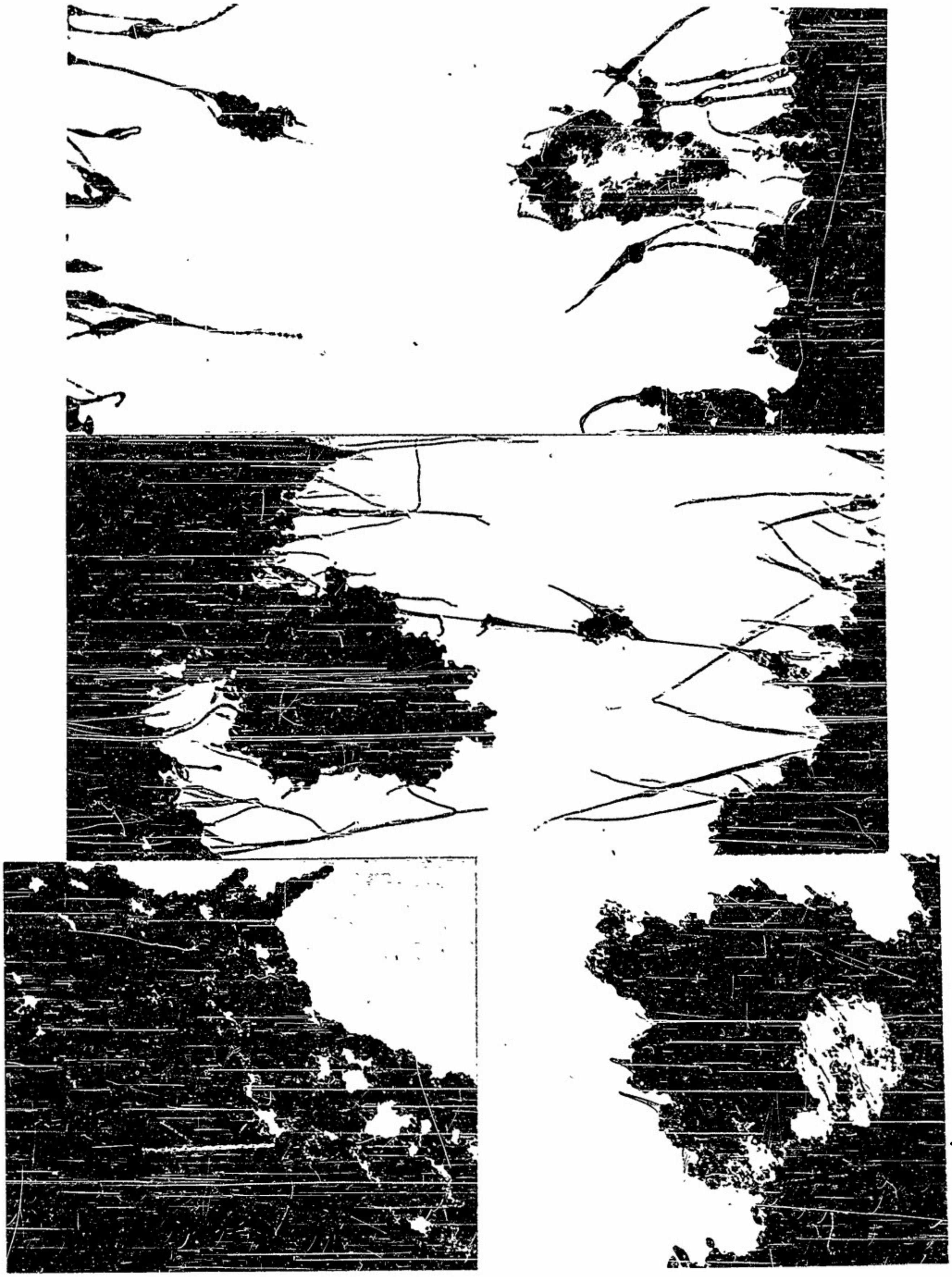
PLATE 11

ELECTRON MICROGRAPHS OF CURED SILICONE RUBBER

CONTAINING ALON AS A PIGMENT

COMPOSITION

G-E 9979-G Gum	100.0
Benzoyl Peroxide	2.0
Alon	98.0



IV. EMULSIFICATION OF SILICONE RUBBER

The interest in emulsification of silicone rubber in the current study is based on the possibility of preparing an emulsion containing both gum and pigment and then breaking the emulsion to produce a very intimate mixture of gum and pigment. This technique is merely a substitute method for milling as a means of dispersing pigment in gum. It has the possible advantage over milling of providing a more intimate mixture. The first interest in this program has involved water as the dispersing medium but it has not yet been possible to obtain a satisfactory emulsion of the gum. The use of an emulsifying agent is indicated but there are certain limits in the nature of this agent. Thus, the sodium salts of fatty acids probably will not be useful because their presence in the final stock would have the effect of lowering the heat resistance of the stock since these acids are less stable to heat than is silicone gum. This same objection may be applied to most of the commercially available emulsifying agents. However, it is possible that the silicone carboxylic acids and sulfonic acids being prepared for use in another part of this program would be useful here also, either as the pure acids or in the form of sodium salts.

A contribution to this attack which has been tried in a preliminary way involves dissolving silicone gum in titanium tetrachloride, in which it appears to be readily soluble. Addition of water to the mixture should result in the hydrolysis of $TiCl_4$ to form TiO_2. Thus, the pigment would be formed as the gum is thrown out of solution. Another possibility in this direction involves the use of silicon tetrachloride, although in this case hydration of the silica might interfere. The possibilities in this general attack are very interesting and will be investigated more thoroughly in the program.

V. REMOVAL OF VOLATILE OILS FROM GUM

It has been suggested that the method of preparing silicone gum is such that the gum might be expected to contain some relatively low-boiling silicone oil. Excessive quantities of low-boiling material would be expected to have an adverse effect on the physical properties of silicone stocks. Removal of these oils must be based on their physical properties, i.e., chemical methods cannot be used because the oils are chemically similar to the gum. Possible methods of removing the oils are solvent extraction, molecular distillation and steam distillation. Some preliminary work has been done on this phase of the program and the investigation is continuing.

VI. CROSS-LINKAGE IN SILICONE RUBBERS

It was noted above that the present method of curing silicone stocks is by the use of benzoyl peroxide. It is assumed, but not definitely established, that the curing reaction involves splitting out of two hydrogen atoms between methyl groups on adjacent silicone chains, resulting in an ethylene bridge between chains. Another type of cross-linking reaction which has been investigated is the cohydrolysis of mixtures of dimethyldichlorosilane and methyltrichlorosilane. This method has not been applied to rubber manufacture. It is generally stated that this scheme results in the creation of simple oxygen cross-links. Considerations based on simple probability theory will show, however, that it is more likely that this cohydrolysis results in relatively long silicone chain cross-links. A third method of cross-linking which has been proposed is oxidation of the side groups on a silicone chain by such agents as air or nitric acid. All three of these methods have the disadvantage that the exact nature of the cross-link formed cannot be stated. To determine whether the method of cross-linking or curing of silicone rubber is an important factor in determining the final properties of the silicone stock, it is essential that methods of curing which result in cross-links of known structure be developed. These methods need not be commercially practicable methods for the purposes of this study, but success with any one of these would lead to attempts to create the same type of cross-link by commercially feasible methods. At the same time, however, possible methods of curing which might not be capable of fundamental analysis should be investigated. This portion of the problem should also be concerned with attempts to decrease the time required for curing of the gum.

Results of curing agent studies which have been performed during this period are presented in Table IV and some of these are plotted in

Figure 12. The conclusions which may be drawn from these test results are:

1. In silicone stocks containing certain pigments a cure results in the absence of an agent added for curing. Specifically, silicone stocks containing 25-volume loadings of Celite 505, Hi-Sil or Micronex W-6 show a definite cure in the absence of peroxide or other curing agent. Furthermore, the cure is reasonably good. The specific property of these pigments which results in the curing action is not known.
2. The effect of using increasing quantities of benzoyl peroxide (1-5% on the gum) in a stock loaded with 25 volumes of Celite 505 is not as marked as might be expected as regards tensile strength. Considering the reproducibility of results, the data could be interpreted as showing essentially no effect on this property. The elongation does decrease appreciably with higher peroxide concentrations and the hardness increases. In the case of an Alon stock the effect on properties of changing benzoyl peroxide concentrations is even less marked.
3. Tertiary butyl perbenzoate gives essentially the same results as benzoyl peroxide in the Celite stock.
4. Di-tertiary butyl peroxide does not function as a curing agent in a Celite 505 stock, the results with this material being essentially the same as those without a curing agent.
5. Rufert nickel (a finely-divided catalytic form of the metal) does not appear to function as a curing agent in Celite stocks, the results showing essentially no better cure than that resulting when no curing agent is added.
6. Raney nickel does not function as a curing agent in Celite stocks.

7. Raney nickel does not "activate" benzoyl peroxide in Celite stocks.

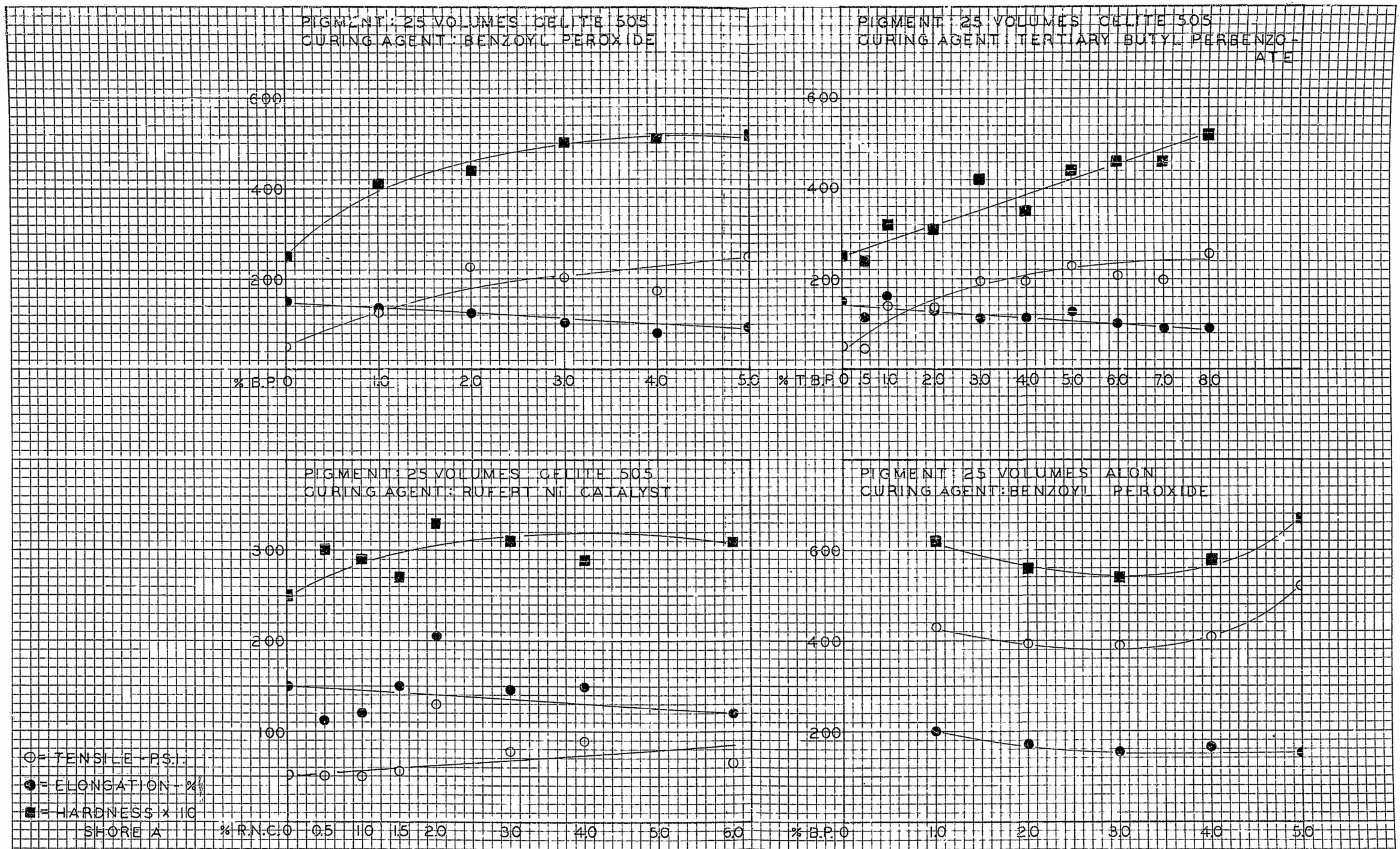
8. p-Trimethylsilylbenzoic acid definitely functions as a curing agent in Celite stocks or in Celite-TiO_2 stocks. This curing action was unexpected and no explanation has been found for it. Investigation of this effect is continuing.

TABLE IV

Curing Agents for Silicone Gum

Pigment	Loading	Curing Agent	% Curing Agent on Gum	Compound No.	Tensile	Elongation	Hardness
Celite 505	25 vol.	None		1274	52	150	25
Hi-Sil	25 vol.	None		1276	155	75	53
Silica 1240	25 vol.	None		1279		-No Cure-	
Rayox 110	25 vol.	None		1277		-No Cure-	
Micronex W-6	25 vol.	None		1278	185	94	49
Celite 505	25 vol.	Benzoyl peroxide	1	1305	125	131	41
"	"	"	2	1072	227	125	44
"	"	"	3	1306	201	106	50
"	"	"	4	1307	176	81	51
"	"	"	5	1308	249	94	52
"	"	tertiary butyl perbenzoate	0.5	1291	45	113	24
"	"		1	1292	140	156	32
"	"	"	2	1293	136	131	31
"	"	"	3	1294	196	113	42
"	"	"	4	1295	194	113	35
"	"	"	5	1296	227	125	44
"	"	"	6	1370	204	100	46
"	"	"	7	1371	198	88	46
"	"	"	8	1372	257	88	52
"	"	di-tert-butyl peroxide	1	1297	32	138	25
"	"	"	2	1298	56	150	26
"	"	"	3	1299		-No Cure-	
"	"	"	4	1300		-No Cure-	

Pigment	Loading	Curing Agent	% Curing Agent on Gum	Compound No.	Tensile	Elongation	Hardness
Celite 505	25 vol.	Rufert Ni (50% fish oil)	0.5	1313	50	113	30
"	"		1	1314	51	119	29
"	"	"	1.5	1315	56	150	27
"	"	"	2	1316	130	206	33
"	"	"	3	1317	77	144	31
"	"	"	4	1318	88	150	29
"	"	"	6	1319	65	119	31
"	"	Raney Ni	1	1340		-No Cure-	
"	"	"	2	1341		-No Cure-	
"	"	"	3	1342		-No Cure-	
"	"	"	4	1343	19	75	28
"	"	"	6	1344		-No Cure-	
"	"	Raney Ni Benzoyl per.	1 1	1345	172	138	42
"	"	Raney Ni Benzoyl per.	2 2	1346	240	113	47
"	"	p-trimethylsilylbenzoic acid	1	1320	122	238	25
			2	1321	177	238	31
Celite 505 TiO_2	100 wt. 75 wt.	"	1	1322	272	75	62
"	"	"	2	1323	350	94	63
Alon	25 vol.	Benzoyl peroxide	1	1324	432	200	62
"	"	"	2	1121	394	169	56
"	"	"	3	1325	389	156	54
"	"	"	4	1303	406	163	58
"	"	"	5	1304	540	125	58



CURING AGENTS IN SILICONE RUBBER COMPOUNDS
FIGURE - 12

CONNECTICUT HARD RUBBER COMPANY U.S. GOVERNMENT CONTRACT DA-44-109-QM-64

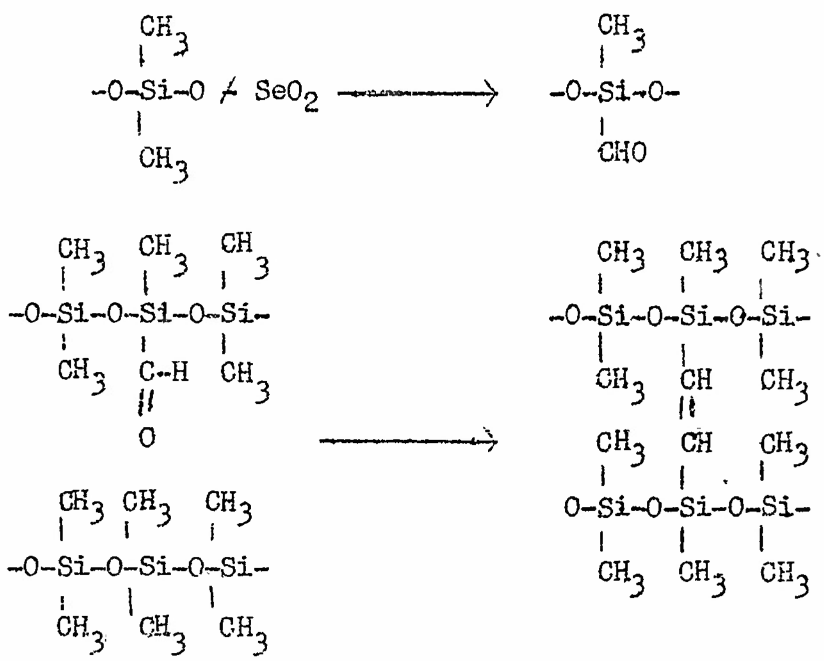
A. Activators for Benzoyl Peroxide.

This portion of the program is concerned with the posibility of increasing the curing rate of silicone stocks by the addition of materials which might function as activators for the benzoyl peroxide. Only Raney nickel has been tried to date and and this was found to have no effect.

B. Oxidation techniques.

The present theory of the effect of benzoyl peroxide on silicone gum involves essentially an oxidation type of reaction. Other methods of curing which depend on oxidation are being sought. The most promising possiblity at the present time is based on the oxidizing properties of selenium dioxide.

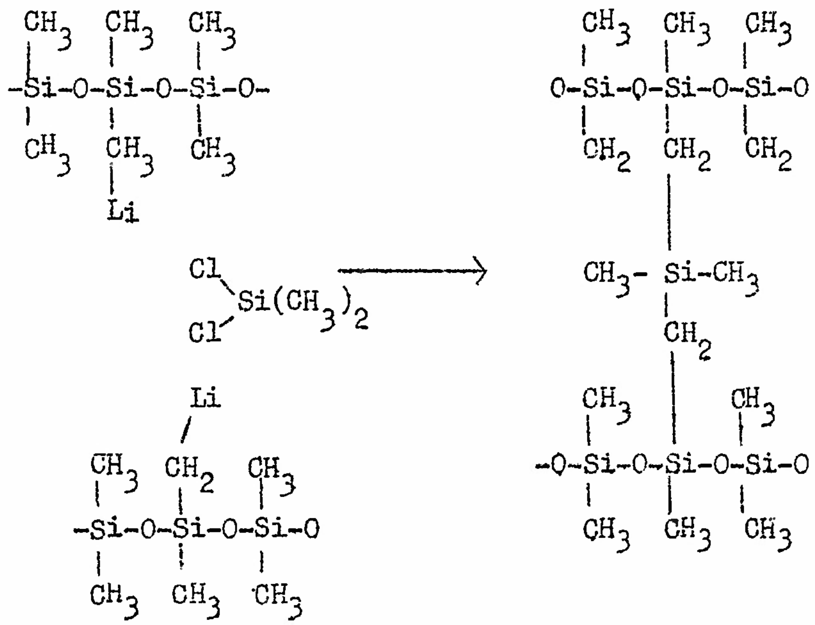
There are theoretical grounds which indicate that the system $\begin{matrix}-C-\\ | \\ -Si-CH_3\end{matrix}$ is analgous to the activation associated with hydrogen atoms in the alpha position to the carbonyl group. Thus, one might expect that the oxidizing action of SeO_2, which converts the system $-\overset{O}{\overset{\|}{C}}-CH_3$ into the dicarbonyl, might be applied to polymethylsiloxane chains to introduce aldehyde functions. The interaction of aldehyde units with active alpha hydrogens could in the presence of SeO_2 (an acidic oxide) lead to aldol-like condensations. The basic chemical reactions are:



In a preliminary exploration of this idea a low molecular weight silicone oil was used to determine whether SeO_2 would react with such materials. General Electric silicone oil 9981LT-35 was found to react with selenium dioxide at elevated temperatures (200-300°C), producing both H_2Se and the free metal. A white semi-crystalline solid in the product can be recrystallized from chloroform. Work on the characterization of this substance is in progress.

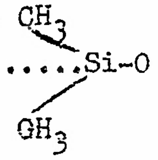
C. Lithium Compounds.

The possibility of using the active metals lithium and magnesium in creating cross-links of known structure is very attractive. Given a silicone chain with some lithium the following type of reaction might be carried out.



Use of other dichloro compounds would result in numberous possible cross links.

A silicone oil boiling within the range 250° - 350° and consisting of a mixture of



chains of average chain lengths equal to ten silicon-oxygen units was chlorinated with the aid of a 600 watt Hanovia mercury arc lamp. The reaction was rapid and exothermic. HCl gas was evolved almost as soon as the mixture of chlorine and silicone was exposed to the ultraviolet light source. The chlorination was stopped as soon as an amount of chlorine substitution had taken place corresponding to three atoms per molecule (ca. ten silicon-oxygen linkages). The chlorinated oil was swept with dry nitrogen, dissolved in ether and the ether solution washed repeatedly with ten percent bicarbonate to remove the last traces of HCl. After the ether solution was washed with water and dried over sodium sulfate, it was allowed to react with lithium.

Lithium ribbon was cut up into small strips about a quarter of an inch square scraped free of grease and added to 250 cc of ether in a three neck flask equipped with a mercury seal, condenser and calcium chloride tube, and dropping funnel connected to a source of nitrogen. After the apparatus was flushed with nitrogen, stirring was commenced and the ether solution of the chlorinated oil added dropwise. No reaction took place under the following conditions:

(a) stirring at room temperature.

(b) stirring in boiling ether.

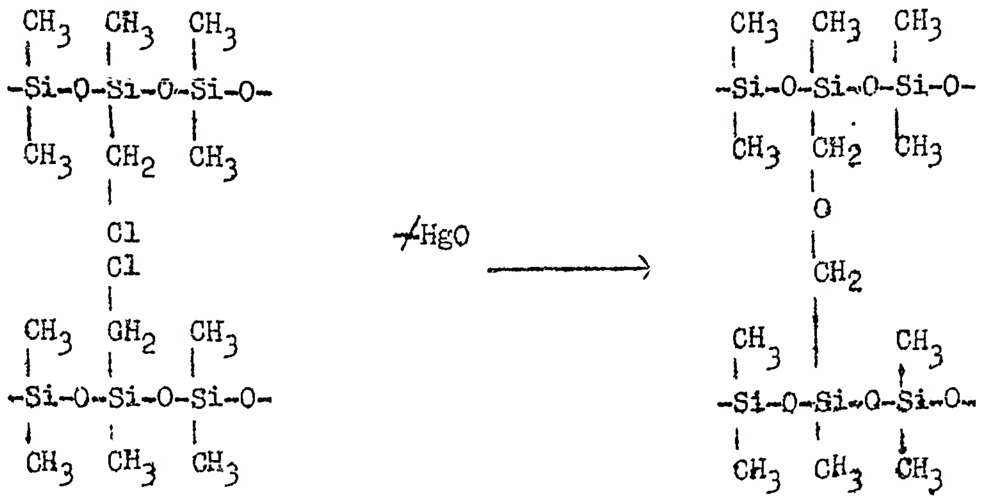
(c) on addition of ethyl bromide.

(d) on addition of ethyl lithium in ether, freshly prepared.

(c) on standing for 72 hours at room temperature.

D. Other Methods

While chlorinated polymethylsiloxane does not appear to react with lithium or magnesium there is a possibility that it would react with a metallic oxide, such as mercuric oxide or lead oxide, to create cross links in the following manner:



Silicone oils of low molecular weight (6-8 atoms of silicon per unit; General Electric silicone oil 9981 LT-4) have been chlorinated under conditions whereby the amount of halogen introduced has been controlled. In the work described below the halogen incorporated has varied from one chlorine per nine molecules of oil to one per three molecules of oil. The halogen content has been kept low so as to keep the model experiments with the oil in line with what would be expected on chlorinating the much higher molecular weight gum.

On heating the chlorinated oil with oxides such as magnesium oxide and zinc oxide no apparent reaction was observed. It may be necessary to use a higher proportion of halogen and to increase the temperature.

The chlorination of 154g. of General Electric silicone oil 9981LT-4 was carried out at a distance of 25 cm. from a Hanovia ultra violet lamp (300 watts) in a Pyrex flask. Under these conditions an immediate reaction took place with rapid evolution of HCl and decolorizing of the yellow mixture. The extent of reaction was measured by noting the weight increase and controlled by the time of halogenation. The number of halogen atoms per molecule (6 to 8 silicon units) was found to be 0.1 after 10 min. and 0.3 after 60 min. The halogenated mixture was flushed with a stream of N_2 to remove HCl. Attempts to react this material with basic oxides are continuing.

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